AD NUMBER
AD200541
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited. Document partially illegible.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 31 MAR 1958. Other requests shall be referred to Air Materiel Command, Wright-Patrerson ABFB, OH 45433.**
AUTHORITY
ASD ltr, 18 Nov 1974

Best

Available

Copy

OMCC-HEF-100
31 MARCH 1958

NO. 14 OF 75 COPIES.

TECHNICAL RESEARCH REPORT

HEADQUARTERS
AIR MATERIEL COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

PREPARATION OF BORON TRICHLORIDE
PART I PRE-PILOT BATCH SCALE

OLIN MATHIESON RESEARCH LABORATORIES

OLIN MATHIESON CHEMICAL CORPORATION
HIGH ENERGY FUELS DIVISION
NIAGARA FALLS, NEW YORK

NOTICES

"The work reported herein was performed in part under Contract NOa(s)52-1023-c for the Bureau of Aeronautics. Control and distribution was transferred to AF 33(600)-33920 by authority of the Bureau of Aeronautics, letter code PP-82 dated 7 November 1956."

OMCC-HEF-100

31 March 1958

TECHNICAL RESEARCH REPORT

PROJECT HEF

No. 14 of 75 copies.

Contract 33(600)-33920
WADC BPS No. 7-(1-3048)-30193
AMC PROJECT 7-558C
United States Air Force
Air Materiel Command

PREPARATION OF BORON TRICHLORIDE
PART I PRE-PILOT BATCH SCALE

Work by: R. Kumagai, P. M. Caro, G. C. Derrick, R. Guibert, P. Allen and J. Giblin

Supervised by: R. Kumagai and P. M. Caro

Written by: G. Commerford, R. Manz, G. C. Derrick and R. Kumagai

APPROVED BY: A. Rose
A. Rose
Fuels Process Development

E. A. Weilmuenster
Director, Fuels Research

"The work reported in this document has been made possible through the joint support and sponsorship extended by the Air Research Development Command and Headquarters, Air Materiel Command under Contract AF 33(600)-33920. It is published for technical information only and does not necessarily represent recommendations or conclusions of the sponsoring agency."

OLIN MATHIESON CHEMICAL CORPORATION

HIGH ENERGY FUELS DIVISION

EXTERNAL DISTRIBUTION LIST C

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

I. SUMMARY

Bench-scale studies were directed toward the development of an economical process for the preparation of boron trichloride by direct chlorination of boric oxide-carbon mixtures at elevated temperatures. Over 200 batch or semi-continuous tests were conducted in 1-inch to 3-inch diameter, vertical-shaft reactors to evaluate such operating variables as formulation, particle size and density of solids feed, bed height, temperature, and chlorine feed rate. Yields, production rates, reaction heat, and extent of by-product formation were determined for optimum operating conditions.

Major obstacles to continuous chlorination were found to be:(a) the softening and fusing tendency of the boric oxide-carbon charge at reaction temperatures, and (b) the formation of a "white solids" complex which condensed out of the reactor effluent gas stream on cooling and tended to plug the system. The first problem was alleviated by the development of a process for preparing spherical feed pellets containing an excess of carbon. Two workable solutions to the second problem were also developed. They were: (a) use of a second reactor containing a hot bed of carbon through which the primary reactor effluent would be passed together with supplementary chlorine to effect conversion of the complex to boron trichloride, and (b) passage of the reactor effluent through a cold column of carbon pellets or boric oxide-carbon pellets to effect condensation and deposition of the "white solids" on the pellets which subsequently could serve as primary reactor feed.

In general, the studies indicated that satisfactory yields and production rates of boron trichloride could be obtained by direct chlorination of boric oxide-carbon particles in a vertical shaft reactor maintained at 1100 to 1500°F. Further studies, preferably with larger equipment, are needed to clarify the heat balance and to determine operability of a continuous moving-bed vertical shaft reactor.

II. INTRODUCTION

In November 1954 bench-scale operations were started for the purpose of investigating process variables encountered in the production of boron trichloride. Information and experience secured from bench scale experimentation were required for the design of a pilot plant. The experimentation was divided into two major categories; Feed Preparation and Reaction. This report covers only the Reaction studies.

Boron trichloride may be prepared by the reaction of molecular chlorine with boric oxide and carbon, anhydrous sodium tetraborate and carbon, or boron carbide, as follows:

$$2B_2O_3 + 3C + 6Cl_2 \longrightarrow 4BCl_3 + 3CO_2 \quad (1)$$

$$CO_2 + C \rightleftharpoons 2CO \quad (2)$$

$$2Na_2B_4O_7 + 14Cl_2 + 7C \longrightarrow 8BCl_3 + 4NaCl + 7CO_2 \quad (3)$$

$$CO_2 + C \rightleftharpoons 2CO \qquad (2)$$

$$B_4C + 6Cl_2 \longrightarrow 4BCl_3 + C \qquad (4)$$

The relative amounts of carbon monoxide and carbon dioxide formed and hence the carbon required is a function of the gas temperature and is related to the equilibrium $CO_2 + C \rightleftharpoons 2CO$. Preliminary cost estimates and feasibility studies indicated that the process of chlorinating a mixture of boric oxide and carbon was the most desirable.

III. EXPERIMENTAL

A. Apparatus

Figure 1 is a process flow sheet illustrating the various pieces of equipment. The reaction and recovery systems are shown in Figure 2. The basic components of the experimental apparatus were as follows: (a) nitrogen and chlorine cylinders, (b) rotameter(s), (c) RA-1, vertical shaft reactor furnace, (d) one or more traps containing glass wool, (e) several laboratory type pyrex condensers and custom made pyrex receivers, (f) a water scrubber, (g) a wet test meter, (h) an Orsat gas analyzer, and (i) glass bubbler tubes containing 10 per-cent potassium iodide.

$$CO + Cl_2 \rightleftharpoons COCl_2 \qquad (6)$$

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl \qquad (7)$$

or $$2BCl_3 + 3H_2O \longrightarrow B_2O_3 + 6HCl \qquad (8)$$

$$Ni + Cl_2 \longrightarrow NiCl_2 \qquad (9)$$

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3 \qquad (10)$$

The effluent gas stream from R-1 first passed through one or more traps containing glass wool which served to filter out any entrained solids, and other solids originating from the decomposition of a complex which contained trichloroboroxole. Downstream from the filter traps were located several pyrex condensers chilled to -60°F or lower which condensed boron trichloride, chlorine, and phosgene. Next, the condenser discharge gas stream was passed through a water scrubber. The purpose of the water scrubber was to recover boron trichloride and phosgene and to remove any hydrogen chloride present in the gas stream. The following reactions occur in the water scrubber:

$$BCl_3 + 3H_2O \longrightarrow 3HCl + H_3BO_3 \qquad (7)$$

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl \qquad (11)$$

$$HCl_{gas} \xrightarrow{H_2O} HCl_{aqueous} \qquad (12)$$

Noncondensable gases discharged from the water scrubber were passed to a wet test meter to measure their volume, and to an Orsat gas analyzer to determine the content of carbon monoxide, carbon dioxide, and oxygen. Finally, the system was vented to the atmosphere.

B. Raw Materials and Preparation of Reactor Feed

A list of the raw materials used to produce boron trichloride along with the analyses and other pertinent data are presented in Table 1.

1. Tablets

The dry materials usually consisting of either boric acid or boric oxide and Witco carbon black (or merely pure Witco carbon for carbon pellets) were mixed by hand. Next, binder consisting of sugar-water, starch-water or chilled pitch was added and the resulting mixture was premixed and then mixed in a Baker-Perkins Sigma type mixing machine. The mixed material was then air-dried to remove excess moisture, remixed in a mechanically powered rotating drum and compressed into 1/4-inch diameter tablets by a Stokes Tabletting Machine. Finally the "green" tablets were sintered at 900 to 1300°F in a muffle furnace to drive off the binder and to convert boric acid to boric oxide. Since the sintered pellets were found to be somewhat hygroscopic, they were stored in sealed glass jars. With proper sintering and materials handling procedures, residual hydrogen contents of not more than 0.3 per cent (equivalent to 2.7 per cent water) were obtained.

2. Briquets

Witco SRF beaded carbon black and boric acid, (the latter had been passed through a micropulverizer), were premixed in a ribbon blender manufactured by the Day Company. Binder, consisting of starch or sugar in water, was added in the mixer directly. Additional carbon or water was added during mixing to produce a material capable of being briquetted. The mixed ingredients were then pressed into briquets with the use of a Komark-Greaves Briquettor. The "green" briquettes were sintered at 900 to 1300°F in a muffle furnace.

3. Spherical Granules

Spherical granules, 1/16- to 3/4-inch in diameter, were prepared by spraying water to a bed of premixed boric acid and Witco carbon contained in an unlined flighted drum which rotated about its longitudinal axis. The wet granules were predried in a rotating drum to eliminate excess moisture after which they were screened. Screened fractions were sintered at 900°F. Precautions were taken to minimize absorption of moisture during storage.

C. Procedure

First, the reactor, R-1 (which was, in most cases a standard 3-inch nps x 12-inch heated pipe) was charged with a boric oxide-carbon feed and this charge was heated to the desired initial operating temperature, usually 1100° to 1500°F. A nitrogen purge was maintained throughout the heating period. After reaching the temperature of test, the nitrogen purge was eliminated and gaseous chlorine was passed to R-1 after passing through a series of driers, and a rotameter. The following reactions occur in R-1:

Main Reaction:

$$2B_2O_3 + 3C + 6Cl_2 \xrightarrow{\Delta} 4BCl_3 + 3CO_2 \qquad (1)$$

and

$$CO_2 + C \rightleftharpoons 2CO \qquad (2)$$

Undesirable Side Reactions

$$BCl_3 + B_2O_3 \longrightarrow (BOCl)_3 \qquad (5)$$

D. Nomenclature Used to Designate Solid Feed Composition

A code was developed in order to designate the formulation of solid feed. An explanation of this code follows.

Boron-containing feed formulation	A-	100	W	20	SuWa	(80Wa)
	↓	↓	↓	↓	↓	↓
item:	1	2	3	4	5	6

item 1 is source of boron:

A = boric acid, H_3BO_3
O = boric oxide, B_2O_3
NBO = Sodium tetraborate, $Na_2B_4O_7$, (anhydrous)
B4C = boron carbide, B_4C

item 2 is per cent excess carbon over the stoichiometric quantity based on the following reaction:

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO \qquad (13)$$

Example: A·100W. If 123.6 g. boric acid (2 moles), which is equivalent to 1 mole of B_2O_3 are used, then 72 g. Witco carbon (6 moles), are added.

item 3 is source of carbon:

W = Witco Chemical Company
Furnace Black: F-1 powder for pellets and SRF beaded black for briquets.
CG = Calcined Gilsonite
PC = Petroleum coke

item 4 is weight per cent of the binder on a wet basis.

item 5 is type of binder:

K-150 = Koppers pitch, m.p., 150°F
K-200 = Koppers pitch, m.p., 200°F
SuWa = Sugar-water
S Wa = Starch-water
M Wa = Industrial molasses-water

item 6 is weight per cent of water in the binder.

E. Chemical Analyses

1. Solid Feed Material

Feed material containing boron and carbon was analyzed for boron, carbon, and hydrogen. In the early phase of bench-scale process development studies, carbon feed (briquets or pellets) was analyzed for carbon and hydrogen only. However, tests showed that a considerable amount of boron was picked up by carbon mixes during mixing and briquetting. Therefore a boron analysis was included. The analytical procedure was as follows. A ground sample contained in a fritted glass crucible was washed with a dilute acid solution. The pH of the filtrate was adjusted prior to addition of mannitol to complex the boric acid, and the resultant solution was titrated with standard sodium hydroxide. A pH meter was used to determine the endpoint. Next the residue was dried at approximately 250°F. The weight of dried residue was reported as per cent carbon. Hydrogen was determined by the standard combustion method utilizing micro or macro techniques.

2. Process Analyses

Figure 3 summarizes the various chemical analyses for chlorination experiments which were required for calculation of material balances, yields, recoveries and over-all stream compositions. Conventional methods were employed. Phosgene was determined by infrared analysis.

F. Electrode Furnaces

1. Electrode Furnace Type I

A drawing depicting the details of the electrode furnace is presented as Figure 4. The electrode furnace, Type I, consisted of six 1-inch diameter graphite electrodes encased in Vycor and inserted into a ceramic or Vycor glass reaction tube. The design of the reactor packing gland permitted linear adjustment of the electrodes to compensate for consumption during reaction. All electrical paths were insulated from metal components. Power to each of the three electrode pairs was controlled by individual 220-volt, single-phase Variacs.

Table II summarizes the work performed with the Type I electrode furnace reactor. All the tablets used for this series of experiments were prepared with Welding Engineers Pitch as binder. The results were unsatisfactory because of an inability to heat the entire furnace to reaction temperature. Preferential current paths were observed in the reactor and the bed was fused after every heating attempt. Contact between the electrode and the pellets was lost periodically and the electrodes had to be inserted further into the tube to regain contact with the bed. Power required to maintain the bed at 1600°F was found to be 250 watts.

The electrode furnace was charged with crushed and sintered feed material so as to attain better contact with electrodes. However, this modification failed to result in improved operation and the bed fused as before. An attempt to obtain better distribution of the heat by passing chlorine through the bed was also unsuccessful.

Two electrodes, each eight inches high and one inch wide, were placed inside the furnace parallel to and opposite each other in order to increase the effective heating volume of the bed. Preferential current and heating paths were again noted but higher temperatures were observed over a greater bed depth. The boric oxide-carbon charge contained in the modified electrode reactor was heated to 1290°F (700°C) in localized areas. However, fusing of the charge persisted. Chlorine was not passed through the bed. A repetition of this experiment produced the same results.

2. Electrode Furnace Type II

A second resistance bed electrode furnace was fabricated. It consisted of a 4-inch inside diameter by 12-inch long Hastelloy pipe lined with a separate piece of Vycor pipe. Each of the three electrodes consisted of an 8-inch high by 1-inch wide by 1/2-inch thick piece of graphite attached to a horizontal 1-inch diameter piece of round graphite which extended through the Vycor and Hastelloy tubes, and through the Vermiculite and Transite insulation to make contact with the power leads. Power was supplied by a 3-phase, 220-volt line with individual variac control to each electrode. The reactor was equipped with three horizontal ceramic thermowells encased in 1/2-inch diameter nickel pipes and spaced 2-1/2-inches above each other.

Results of a calibration experiment with sintered carbon pellets as the charge are shown in Table III. Approximately one and one-half hours were required to raise the bed temperature to 1100°F. The power necessary to maintain that temperature was 757 watts. Power required to maintain a temperature of 1300°F was 956 watts.

Chlorination experiments were not conducted with this furnace because work had been initiated on another reactor system which seemed more promising.

G. Externally Heated Reactor (Resistance Wire-Heated)

Figure 5 is an illustration of the resistance wire furnace used. Nichrome wire covered 8 inches of the 12-inch effective heating zone. The reactor design permitted intermittent manual feeding of solid feed as well as intermittent bottoms removal. The reactor parts were fabricated from nickel or high nickel alloy except the feed and ash removal valves which were cast iron. This design enabled the replacement of a defective reactor tube without replacing or modifying the furnace headers.

Initially, a 51-mm. Vycor tube was wrapped with Nichrome wire having a resistance of 20 ohms. Power was supplied through a 220-volt variac. This furnace containing boric oxide-carbon tablets was heated to 1320°F for one hour and the bed was not fused when examined.

The Vycor tube, however, was found to be fractured and it was replaced with a 2-inch n.p.s. nickel pipe, schedule 40. Shorting of the resistance wires was minimized by imbedding them in alundum cement. This reactor was quite durable and was operated for as many as six experiments before the wires short circuited. The two-inch nickel reactor was replaced with a 3-inch nickel pipe. One chlorination experiment was conducted with use of a 4-inch reactor plus the general equipment shown in Figures 1 and 2.

During most of the experiments boric oxide-carbon pellets were fed semi-continuously to the primary chlorinator, R-1. At intervals a combination bed level bed-packing tool was inserted at the top of the reactor, to pack the bed and check the level. Additional feed was added to bring the bed up to the original level and ash was periodically withdrawn through the bottom valve. The incorporation of a double-valve, air lock feeding system eliminated the necessity of turning off the chlorine during bed level checks, packing of the bed, or charging of fresh boric oxide-carbon feed. Operating instructions called for continuous operation until difficulties such as excessive leakage due to plugs in the reactor bed or effluent gas stream or corrosion of metal components forced termination of the experiment. Tables IV and V summarize the results of the preliminary process-development chlorination experiments.

IV. PROCESS VARIABLES

A. Production Rate vs. Chlorine Rate

Figure 6 is a plot of chlorine rate vs. boron trichloride production rate. A production rate of 90 lb./hr./ft.^{3} of charge (4.4 lb. BCl_3/hr. for a 12-inch x 3-inch diameter bed) was attained at a chlorine rate of 34 cu.ft./hr. at S.T.P. (BL-26), and chlorine did not appear in the effluent until 9 minutes after start-up. Chlorine rates higher than 34 cu.ft./hr. at S.T.P. were not attempted because of the inadequacy of the recovery system. Assuming 50 per-cent void space in the bed under the conditions of BL-26, the minimum residence time of chlorine in the heated bed was calculated as 0.25 second.

B. Feed Formulation

Figure 7 shows the effect of varying amounts of excess carbon on the boron trichloride production rate vs. chlorine rate curve for full-bed (12-inch solid feed) experiments. To eliminate any interaction due to reaction temperature, only data in the temperature range 1307 to 1364°F are plotted. A single exception to this temperature limitation is one point at 1242°F. Figure 7 shows that the amount of excess carbon, ranging from 20 to 200 per cent, has an insignificant effect on the production rate.

C. Relative Reactivity of Boric Acid and Boric Oxide Base Pellets

A series of chlorination experiments were performed to determine the relative reactivity of boric oxide and boric acid base pellets. In each case the pellets charged to the reactor R-1 were sintered to convert boric acid to boric oxide and to drive off the binder. The results of these experiments are presented in Figure 7, Boron Trichloride rate versus Chlorine rate. Comparing the curve for A-100W-25k. 150 feed with those for boric oxide base pellets, it is apparent that there is an insignificant difference between acid and oxide as a starting material with respect to boron trichloride production rate.

D. Effect of Temperature

The data plotted in Figure 6 (production rate vs. chlorine rate) are for chlorination experiments made in the temperature range 1150° to 1593°F. There does not appear to be any significant discrepancy in the data plotted for the line which cannot be attributed to experimental error. Process development studies performed by the Chemical Research Department (Olin Mathieson Chemical Corporation) indicated that the advantages of preparing boron trichloride at 1740°F rather than 1020°F are threefold: (a) the rate of reaction is faster, (b) the period of complete chlorine conversion is longer, and (c) there appears to be less solid intermediate ("white solids") deposited in the effluent gas lines.

A plot of chlorine conversion vs. initial bed temperature for feeds containing various amounts of excess carbon is presented in Figure 8. The data for each level of excess carbon exhibits a high degree of experimental scatter. If any possible influence of excess carbon is ignored the resulting line indicates that increasing the initial bed temperature produces an increase in the chlorine pass yield conversion. For experiments at higher temperatures, the volume(depth) of bed necessary to preheat the incoming cold chlorine was less than that required for experiments at relatively low temperatures. Consequently it is believed that part of the increased boron trichloride production rate of higher temperatures is attributed to the gain of "effective heated volume of the bed". Additional experiments to establish the effect of temperature more accurately were not made because of the urgent needs to evaluate other process variables.

E. Effect of Bed Height

The reactor bed height appears to be a very important variable. Figure 9 depicts the relationship between boron trichloride production rate, lb./hr./ft.^{3} of charge and chlorine rate for several bed heights. This figure shows that higher production rates are experienced for smaller bed heights. Figure 10 illustrates the effect of bed height on boron trichloride production rate at several levels of chlorine throughout and this plot also shows the substantially higher production rates at lower bed levels.

Although lower bed heights result in increased boron trichloride production on a lb./hr./ft.^{3} of charge basis, this increase is attained at the expense of lower chlorine conversions. This supposition is illustrated in Figure 11: "Chlorine Conversion vs. Chlorine Rate for Three-, Six-, and Twelve-Inch Bed Heights". Referring to this figure the following chlorine conversions are noted for 10 cu.ft./hr. at S.T.P. of chlorine: twelve-inch bed, 59 per cent; six-inch bed, 53.5 per cent, and three-inch bed, 41 per cent.

F. Recoveries and Yields

In Table V, the recoveries and pass yields are summarized. The per-cent recovery does not total 100 per cent because of such factors as: (a) inaccurate rotameter readings; (b) leaks in the recovery system; and (c) incomplete samplings. For full-bed (12 inches) experiments, the following average values were calculated:

Boron			Chlorine		
Pass Yield per cent	Overall Yield per cent	Recovery per cent	Pass Yield per cent	Recovery per cent	Cl_2 in Condensed Product per cent
29	50	73	65	84	0.5 to 20.

The low boron pass yield is attributed to incomplete reaction and to bormation of white solids. The difference between chlorine recovery and chlorine pass yield represents Cl^- as hydrogen chloride and condensed free chlorine. Although the purity of the product shows a considerable range for free chlorine content, approximately 25 per cent of the full-bed experiments yielded condensed product with a free chlorine content of less than 1 per cent. Condensed product from the preliminary process-development experiments was not analyzed for phosgene. However, the phosgene content of condensed product from experiments using boric oxide-carbon briquets as R-1 solid feed was between 0.0 and 0.9 per cent.

G. Formation of "White Solids"

Reference to the "remarks" column, Table V, shows that quite a few experiments were terminated because of the formation of plugs in the reactor effluent gas lines. These plugs were caused by formation of fluffy white material designated as "white solids". To prevent these solids from collecting in the spirals of the product condensers, glass wool was inserted in the 2-inch pyrex effluent gas line to serve as a filter. The presence of these solids may be attributed to the formation of a complex which contained trichloroboroxine, which according to the literature, decomposes very rapidly and gives off hydrogen chloride when exposed to the atmosphere (1).

Table VI lists the compositions of the solids found in the effluent gas lines for experiments 450D-48 and BL-1 to 25. Solids were exposed to the atmosphere during sampling and sample preparation. These data are presented graphically in Figure 12. Indications are that larger concentrations of boric oxide are present at the higher chlorine rates. Table VII is a compilation of weight of boron in boron trichloride produced divided by weight of boron in the "white solids". An attempt to correlate the B_{BCl_3} to $B_{\text{white solids}}$ ratio with chlorine rate, temperature and bed level was not successful due to scatter of the data. However, Figure 13, "Effect of Chlorine Rate on B_{BCl_3} to $B_{\text{white solids}}$ Ratio" suggests that greater boron conversion (to boron trichloride) is attained at higher chlorine rates. The data contained in Table VII indicate that, on the average, a B_{BCl_3} to $B_{\text{white solids}}$ ratio of 14 may be expected.

"White solids" were synthesized in the laboratory by passing boron trichloride through a bed of dry boric oxide at temperatures as low as 570°F. Nitrogen or chlorine did not produce "white solids" when passed through boric oxide which shows that these solids are not entrained. When a portion of the synthesized solids were heated to 1110°F (600°C), they did not sublime but instead formed a sticky mass presumed to be molten boric oxide.

(1) "Trichloroboroxole", Goubeau and Keller, Z anorg. u. algem. chem. 265, pp. 73-89, 1951.

An air free sample of "white solids" was obtained using a one-inch Vycor tube containing pelletized boric-oxide-carbon feed heated by a split element resistance wire furnace. This sample yielded a boric oxide to boron trichloride ratio of 3.06 to 1, which does not correspond to the 1 1 ratio of trichloroboroxine.

Various attempts were made to eliminate or decrease the amount of 'white solids" formed. A reactor containing 300 per cent excess carbon failed to effect a reduction.

The solids deposited in the effluent gas lines were not always white, on many occasions they were contaminated by appreciable amounts of chlorides of nickel and iron. Compositions of solids collected in the effluent gas lines during experiments BL-28 to 33 are shown in Table VIII.

"White solids" caused severe operating difficulties because they plugged the gas lines. It is believed that the boron trichloride produced in the chlorinator reacts with boric oxide in the feed to form the compound trichloroboroxine, or $B_3O_3Cl_3$ which deposits out of the gas stream at approximately 570°. The compound when decomposed, liberates boron trichloride and deposits boric oxide containing a portion of trapped boron trichloride b.p. 54.5°F as white solids.

H. Formation of Hydrochloric Acid

Even for experiments at low chlorine rates showing very little chlorine in the condensed product, the chlorine pass yield (conversion) was significantly less than the chlorine recovery; for example in experiment BL-10 at 9.5 cu.ft./hr. at S.T.P. of chlorine, there was 0.29 per cent chlorine in the condensed product, chlorine recovery was 76.7 per cent and chlorine conversion was 65.6 per cent. Infrared and mass spectrographic analyses of the reactor effluent gas indicated the presence of 10 to 30 per cent hydrogen chloride. These results were substantiated by the presence of Cl^- in the water scrubber in considerable quantities above the stoichiometric equivalent of the boron content. For a boric oxide-carbon pellet feed containing 11 per cent boron (B_2O_3) and only 0.2 per cent hydrogen (water) the chlorine conversion is reduced by 6.7 per cent in accordance with the reaction:

$$2BCl_3 + 3H_2O \longrightarrow B_2O_3 + 6HCl \qquad (8)$$

The detrimental effect of relatively small quantities of residual (after sintering) hydrogen, in reducing boron and chlorine conversions, contributing to "white solids" formation, and indirectly increasing corrosion, has been recognized. Therefore, appropriate precautions were taken in storage, sintering, and handling to prevent absorption of moisture. Sintering experiments indicated that it was almost impossible to reduce the residual hydrogen content to a level less than 0.1 per cent (0.9 per cent water) and that increasing the sintering temperature from 900 to 1300°F not only failed to reduce the hydrogen content, but also increased the boron and carbon losses.

The average hydrogen chloride-boron trichloride weight ratio for eight randomly chosen full-bed experiments was 0.38; hydrogen chloride-boron trichloride weight ratios for these experiments are presented in Table IX. The highest hydrogen chloride-boron trichloride ratio of the eight experiments was exhibited by BL-18, 0.629, and the lowest by BL-19, 0.232.

I. **Carbon Monoxide-Carbon Dioxide Ratio in the Vent Gas Mechanism of the Reaction**

The carbon monoxide-carbon dioxide ratios obtained in the vent gases for these experiments are shown in Table X and Figure 14. The latter includes curves for the theroetical carbon dioxide-carbon monoxide equilibrium (2) relationship with and without the dilutive effect of boron trichloride. Figure 14 shows that the presence of boron trichloride or any other diluent such as phosgene, hydrogen chloride, or free chlorine tends to displace the carbon monoxide-carbon dioxide vs. temperature curve to higher ratios.

The exact mechanism of the reaction is not known. It is believed that the reaction proceeds by one of two paths

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO \qquad (\mathrm{II})$$

finally $$CO_2 + C \rightleftharpoons 2CO \qquad (2)$$

or $$2B_2O_3 + 3C + 6Cl_2 \longrightarrow 4BCl_3 + 3CO_2 \qquad (\mathrm{I})$$

$$CO_2 + C \rightleftharpoons 2CO \qquad (2)$$

Figure 14 shows that increasing the bed height (longer residence time for $CO_2 + C \rightleftharpoons 2CO$ equilibrium), causes an increase in carbon monoxide-carbon dioxide ratio. This observation suggests that carbon dioxide rather than carbon monoxide is formed first, equation (I). Cleveland Industrial Research, a subcontractor, reported that hot boric oxide did not chlorinate when subjected to a mixed stream of carbon monoxide and chlorine.

The data contained in Figure 14 indicate that carbon dioxide and not carbon monoxide is formed initially and hence reaction (I) occurs. The higher than theoretical carbon monoxide-carbon dioxide ratios for 12-inch beds may be attributed to the presence of hydrogen chloride and/or phosgene in the reactor effluent gas stream.

J. Bed-Movement

By far the most serious operating difficulty experienced during the foregoing semi-continuous and subsequent batch chlorination experiments was the failure of the bed to drop even after it was almost thoroughly chlorinated. An examination of the reactor bed prior to passage of chlorine, by probing with a metal rod always showed it to be soft or fused. This characteristic, is attributed to the physical characteristics of amorphous boric oxide. The amorphous form has no definite melting point. At 750°F, amorphous boric oxide softens sufficiently to be mechanically deformed; at 1110 to 1290°F, the viscosity is reduced so that extrusion is possible; and at temperatures above 1440°F, it melts. Consequently softening of the bed to some extent is almost unavoidable. To alleviate softening and fusing, the solid charge for most chlorination experiments contained a considerable amount of excess carbon. Attempts to correlate bed movement difficulties with chlorine rate and bed temperature were not successful.

V. USE OF A CARBON BED TO CONVERT WHITE SOLIDS

A. Discussion

The "white solids" formed along with boron trichloride resulted in plugging of the effluent gas lines necessitating frequent shut down, and reduction in chlorine and boron conversions. Solid accumulating in the lines would prevent continuous operation of a commercial size reactor. It was believed that since the "white solids" appeared to be boric oxide they could be reacted in the presence of carbon and supplementary chlorine to form additional boron trichloride. An extensive test program was initiated to determine (a) the feasibility of using a carbon bed, and (b) the optimum size of carbon bed for white solids conversion. All the carbon bed experiments were of the "batch" type.

At first a 1-inch diameter x 12-inch long horizontal auxiliary carbon bed was installed immediately downstream from the reactor. Experiments BL-34 to 41 were conducted with this addition. The results were not conclusive. In a second set of experiments, carbon pellets were charged directly into a 3-inch inside diameter by 12-inch (heated length) chlorinator on top of a charge of boric oxide-carbon pellets. The results of these special experiments (A-1, 2 and 6) were so encouraging as to warrant fabrication of a 2-1/2-inch inside diameter x 24-inch long carbon bed reactor. Experiments BL-45 to 56 were made with this larger carbon bed in a horizontal position. Excessive channeling through the carbon bed necessitated the installation of a vertical carbon bed. Thirty-one batch chlorination experiments (BL-57 to 83) were made in the 2-1/2-inch inside diameter by 24-inch long (heated) vertical bed. Chlorine rate and carbon bed level were varied to obtain design data. Experiments BL-84 to 91 were performed to determine the effect of feed formulation (per cent excess carbon) on production rate. Except for a few control experiments a separate stream of chlorine was passed to the carbon bed. The results of the carbon bed experiments are summarized in Tables XI, XII, and XIII

B. One-Inch Inside Diameter Horizontal Carbon Bed

The apparatus utilized for this series of experiments, BL-34 to 41, was essentially the same as that used for the preliminary process-development studies as illustrated in Figures 1 and 2. A 1-inch inside diameter by 12-inch long horizontal carbon bed tube was installed at the 1-inch nickel pipe section of the chlorination reactor effluent gas header. The carbon bed charge consisted of carbon (Witco) pellets and was heated to approximately 1300°F. A supplemental chlorine stream was passed to the carbon bed, R-2. The R-2/R-1 chlorine feed ratio was [illegible].2.

In general, the operating procedure was the same as that used for the preliminary process-development studies. However, since these experiments were batch type, boric oxide-carbon feed material was not charged during the experiment. Operating instructions were to pass chlorine until free chlorine appeared in the effluent gas stream as indicated by color change of a 10 per-cent potassium iodide bubbler, or until excessive pressure or any other operating failure forced termination.

Figure 15 compares the production rate vs. chlorine rate curve for the 1-inch x 12-inch carbon bed experiments with corresponding curves for the preliminary process-development experiments. Two 1 x 12-inch carbon bed production rate curves are shown, one based on the chlorine rate to the primary reactor R-1, and the other based on total chlorine rate to R-1 and R-2. A comparison of the regular experiment (no carbon bed) curve with that for 1 x 12-inch carbon bed experiments based on chlorine rate of R-1 only, indicates that additional conversion occurred in the carbon bed (R-2). However, with the total chlorine rate as a basis, it was apparent that most of the chlorine fed to R-2 was not undergoing reaction. Also, the average chlorine conversion for the 1 x 12 horizontal carbon bed experiments, 54.1 per cent, was lower than that for regular experiments, 65 per cent. The average ratio of boron in boron trichloride to boron in white solids was 11.5 which does not represent an improvement over the ratio, 14, obtained for the earlier experiments.

The effluent gas velocity was increased 9-fold in the 1-inch inside diameter carbon bed after passing from the 3-inch inside diameter, primary reactor, R-1. The short residence time apparently was not sufficient to permit conversion of the solids. The auxiliary carbon bed was then charged directly into the heated zone of the reactor on top of the boric oxide-carbon charge to determine the effectiveness of a carbon bed in a 3-inch diameter reactor.

C. Layer of Carbon Pellets on Top of Boric Oxide-Carbon Pellets

The apparatus used was the same as that for the preliminary process-development studies.

First, boric oxide base pellets containing 100 per cent excess Witco carbon were charged to R-1 so that a 3-inch tall bed was contained in the hot zone. On top of this feed, a 3- or 9-inch layer of Witco carbon pellets was added to serve as the carbon bed. Chlorine at the relatively high rate of 20 cu. ft./hr. at S.T.P. was passed to R-1 until the [illegible] was assumed to be exhausted based on predetermined calculations or until operating difficulties forced termination of the experiment.

The average production rate for experiments BL-Sp. Exp. A_1, A_2, and A_3, 142 lb./hr./ft.^{3} of bed (Table XII), (based on a 3-inch diameter x 3-inch high bed) was greater than the calculated for a 3-inch reactor bed height without a carbon bed, 130 lb./hr./ft.^{3} of charge using an extrapolation of the data presented in Figure 9. In view of these encouraging results, a 2-1/2-inch inside diameter x 24-inch long horizontal carbon bed secondary reactor was fabricated for further carbon bed experimentation.

D. 2-1/2-Inch Inside Diameter by 24-Inch Horizontal Carbon Bed

The reaction, carbon bed, and solids recovery section of the apparatus used for experiments BL-45 to 56 are illustrated in Figure 16. The resistance wire-heated R-1 used for previous experiments was replaced with a gas-fired reactor of the same dimensions (3-inch n.p.s. x 12 inches long). Carbon pellets in the nickel carbon bed reactor were replaced after ever 3 experiments. The solids trap assembly depicted in Figure 16 was found to be ineffective and was replaced with a 2-inch diameter pyrex pipe containing glass wool. No changes were made in the recovery system illustrated in Figures 1 and 2.

Chlorine flow was maintained until free chlorine appeared in the reactor effluent or until a termination was necessitated by operational difficulties. The R-2/R-1 + R-2 chlorine rate was varied between 0.1 and 0.2. With the exception of BL-45, in which A-100CW feed material was used, the primary reactor charge consisted of A-100 W sintered pellets.

In Figure 15 the production rate vs. chlorine rate data are plotted with the use of both the chlorine rate to R-1 only and total chlorine rate as a basis. Both curves exhibit boron trichloride rates significantly higher than that for the regular (no carbon bed) experiments. These data indicate that virtually all of the R-2 chlorine feed reacted with the "white solids" or complex to form additional boron trichloride. This observation was substaintiated by the increased average chlorine conversion (72 per cent) as opposed to 59 to 65 per cent for the regular experiments.

Although the 2-1/2 x 24- inch horizontal carbon bed appeared to be effective in converting the complex, some uncertainty existed. A single control experiment (no carbon bed), BL-51, gave results which seemed to discredit the effectiveness. The installation of the gas-fired reactor reduced the height of the effective heated reaction zone from 12 inches to approximately 10 inches. Consequently, production rate data for experiments BL-45 to 56 are based on a 10-inch rather than 12-inch bed height. Calculating the production rate data on a 12-inch rather than 10-inch basis would cause the 2-1/2 inch carbon curve to regress toward the regular experiment curve. It is safe to assume that a considerable amount of channeling occured. That is, the carbon pellets would have a tendency to settle thus permitting part of the R-1 effluent gas to pass through the carbon bed without contacting the carbon pellets. Therefore, a vertical carbon bed was installed.

E. 2-1/2 Inch Inside Diameter by 24-Inch Vertical Carbon Bed

The reaction section for this series of experiments was identical with that used for the 2-1/2 inch inside diameter horizontal carbon bed experiments except that the carbon bed was vertical and a heat exchanger was installed between the primary reactor, (R-1) and the carbon bed, (R-2). This heat exchanger which used hot flue gas from the gas fired R-1 was incorporated to prevent deposition of white solids between R-1 and R-2. No changes were made in the recovery system.

Beginning with this series of experiments the method of charging the bed was changed. Heretofore the cold zone (pipe section below the hot zone) contained boric oxide-carbon feed material. From BL-57 on, carbon pellets were first charged to R-1 up to 1 inch above the bottom of the Transite shell. Eleven inches of boric oxide-carbon pellets or briquets were then charged to R-1 on top of the carbon pellet layer. The 2-1/2 inch inside diameter x 24-inch long carbon bed was filled with fresh carbon pellets for each experiment. The height of the carbon bed was varied from 0 to 24 inches. A stream of chlorine amounting to between 10 and 20 per cent of the R-1 rate was passed to the carbon bed. For experiments in which no carbon pellets were used, a small amount of chlorine was fed directly to R-2 for the purpose of duplicating a chlorine atmosphere. The carbon bed charge was supported by a slotted spool piece inserted through the bottom flange so as to contain the entire bed in the hot zone. Experiments were terminated when free chlorine appeared in the R-2 effluent gas stream or when operating difficulties (high pressure, leaks) necessitated shut-down.

The effect of carbon bed height on boron trichloride production rate vs. R-1 chlorine rate is depicted in Figure 17. A production rate curve for the preliminary process development studies is included for comparison. Figure 17 shows that a considerable portion of the carbon bed chlorine stream reacted to form additional boron trichloride. Table XI shows that many experiments of this series continued for fairly long periods before chlorine was detected in the carbon bed effluent gas stream. This indicates that, during this period, all of the supplemental chlorine fed to the carbon bed reacted with the trichloroboroxine and carbon to form boron trichloride. . Again, this supposition is substantiated by Figure 17, which shows that for 9, 12, and 24 inch x 2 1/2 inch inside diameter carbon beds, the boron trichloride production rate is increased approximately 20 per cent. Figure 18, production rate vs total (R-1 and R-2) chlorine rate again shows that for 9-, 12-, and 24-inch carbon bed heights, essentially all of the carbon bed chlorine was converted to boron trichloride.

The effectiveness of the carbon bed is further demonstrated by the highly significant increase in the $B_{BCl_3}/B_{\text{white solids}}$ ratio, which averaged approximately 89 as compared with the ratio of 8.5 for the five control experiments BL-57, 67, 72, 72R and 73.

Figure 19 is a plot of the effect of carbon bed height on production rate of boron trichloride. Considering the nature of the curves shown in Figure 19 and the surprisingly high chlorine conversions exhibited by a 6-inch carbon bed, it is felt that a 12 inch long x 2-1/2 inch inside diameter bed (0.0324 ft.^{3}) is of sufficient size to convert the complex, at a R-1 chlorine rate of 18 cu.ft./hr. at S.T.P. The boron trichloride production rate at 18 cu.ft./hr. at S.T.P. is approximately 62 lb./hr./ft.^{3} of R-1 charge which is equivalent to 2.79 lb./hr. boron trichloride based on the 3 inch diameter x 11 inch high R-1 bed. Dividing the volume of the carbon bed, 0.032 ft.^{3} by the boron trichloride production rate 2.79 lb./hr. yields a design value of 0.012 ft.^{3} of carbon bed per pound per hour of boron trichloride produced.

The low boron pass yields, which average approximately 45 per cent, may be attributed to the operating procedure which called for termination of the experiments at the first appearance of free chlorine in the R-2 effluent gas stream.

Reference in Table XII shows that the phosgene content of the condensed product ranged from a low of 0.0 to a high of 1.8 per cent. Phosgene is formed by the reaction

$$CO + Cl_2 \rightleftharpoons COCl_2 \qquad (6)$$

Above approximately 1470°F (800°C) the reaction favors total decomposition of phosgene. However, results shown in Table XII indicate no correlation between carbon bed temperatures in the range 1300-1600°F and phosgene formation. Phosgene formation was highest for experiments in which the 25-inch carbon bed reactor was maintained empty (zero carbon bed) or partially full (6-inch carbon bed). The apparent conclusion is that the combination of a hot empty tube and a reactor gas stream containing free chlorine and carbon monoxide is conductive to formation of phosgene.

The average hydrogen chloride to boron trichloride weight ratio for control experiments (BL-57, 67, 72, 73 and 72R) and 24-inch carbon bed experiments was 0.11 and 0.15 respectively, which represents a substantial improvement over the average value of 0.38 obtained for the preliminary development experiments. The hydrogen content of the boric oxide-carbon feed for the carbon bed control experiments averaged 0.35 per cent whereas the percentage in the boric oxide-carbon feed for the preliminary development experiments was higher than 1.3 in some cases.

F. Effect of Excess Carbon in Feed

Several experiments (BL-84 to 91) were performed to determine the effect of excess carbon content of the feed on its reactivity. Previously, experiments had been performed to investigate this variable as part of the preliminary process development studies. These early experiments had indicated that increasing the excess carbon from 20 per cent to 200 per cent (over the stoichiometric amount to form carbon monoxide) had very little effect on the production rate and on the amount of "white solids" formed. The results for experiments BL-84 to -91 are presented in Tables XI and XII.

A summary of the results showing average yields and production rates obtained with various formulations are shown in the following table.

Excess Carbon in Feed per cent	Production Rate (a) lb./hr./$ft.^3$	Pass Yield (Conversion) B per cent	Pass Yield (Conversion) Cl per cent	Overall Yield
50	48.0	81.2	79.7	94.1
100	45.0	62.4	77.2	95.1
200	40.3	85.3	71.2	97.3
300	41.6	77.9(b)	75.7	85.7

(a) Based on 14.1 cu.ft./hr. at S.T.P.
(b) Low because of hole in thermowell requiring shutdown.

The data show both production rates and chlorine conversions decreased with an increase in the excess carbon content of feed. Inasmuch as conditions were about the same with respect to temperature, residence time of chlorine, and experiment time, it is believed that the lower excess carbon feed provided more efficient contact of the active solids by chlorine. The bulk densities of the various feed materials are shown in Figure 20.

G. Grate Experiments

The practice of supporting the R-1 bed by a bed of carbon pellets would hinder the continuous removal of ash and carbon. It was felt that the use of grate might overcome this difficulty and, at the same time, definitely locate the reaction zone.

Accordingly a slotted grate was installed in R-1 to replace the bed of carbon pellets. Aside from this modification, the apparatus and operating procedure was the same as that for the 2-1/2 x 24-inch vertical carbon bed experiments.

The results of a single experiment, BL-75, indicated that loss of the preheating action normally supplied by the supporting pellets was the cause of a decrease in production rate and boron pass yield. Visual examination of the reactor bottoms showed a lightly fused mass of unreacted briquets located just above the grate.

VI. RELATIVE REACTIVITY OF VARIOUS SOLID FEED FORMS

Studies were conducted to evaluate the relative reactivities of the following feed forms

a. Tablets
b. Briquets
c. Spherical Granules
d. Powder

Reaction characteristics of tabletted feed were reported in the preliminary process development studies.

A. Reaction Characteristics of Briquetted Feed

Experiments BL-57, 67, 72, 72R and 73 (briquetted feed, control - no carbon bed), summarized in Tables XI, XII, and XIII are used to compare the relative reactivity of briquetted versus pelletized feed. Figure 17, shows a comparison of briquetted feed (control, no carbon bed) with tabletted feed (preliminary process development experiments) with respect to boron trichloride production rates. This illustration shows that at a give rate of chlorine flow, solid feed in briquet and pellet form produced boron trichloride at substantially the same rate. For convenience the following table is presented to compare the reaction characteristics of briquetted feed with pelletized feed.

	Boron			Chlorine		Impurities in Condensed Product	
Feed	Pass Yield per cent	Overall Yield per cent	Recovery per cent	Pass Yield per cent	Recovery per cent	Cl_2 per cent	$COCl_2$ per cent
Pellets	29(a)	50	73	65	84	0.5 → 20	Not analyzed
Briquets	44	72	78	62	83	6. → 27.	0.0 to 0.9

Feed	Production Rate (b) lb./hr. BCl_3	B_{BCl_3}/B_{solids} Wt. Ratio	HCL / BCl_3 Wt. Ratio
Pellets	1.99	14	0.38
Briquets	2.07	8.3	0.11

(a) Relatively low because of BOC pellets in cold zone.
(b) Based on Cl_2 rate of 15 cu.ft./hr. at S.T.P. to R-1

A comparison of the average boron pass yields is not advisable because of the different charging procedures used. The foregoing table shows that briquets and pellets exhibit almost identical chlorine conversions. The difference in $B_{BCl_3}/B_{white\ solids}$ ratio (14 vs. 8) is not considered significant. It was pointed out previously that the lower hydrogen chloride-boron trichloride average ratio for the carbon bed control experiments (chlorination of boric oxide-carbon briquets, no carbon bed), 0.11, as compared with 0.38 for BL experiments with pelletized feed (hydrogen chloride - boron trichloride = 0.38) was the result of lower residual hydrogen content of the solid feed.

The comparable reactivities of briquetted feed and tabletted feed indicate that reactivities were not affected by difference in particle diameter between 1/4 inch (pellets) and 3/4 inch (briquets). Also significant is the fact that briquets exhibited good reaction characteristics in spite of the adverse "mean particle diameter÷reactor diameter" ratio of 3/4÷3, or 0.25.

B. Reaction Characteristics of Spherical Feed

A gas fired 3-inch inside diameter x 12-inch externally heated primary chlorinator R-1, and a 2-1/2 inch inside diameter x 24-inch long vertical carbon bed, R-2, were used for this series of experiments, BL-108 to 138R. The effluent gases from R-1 entered the bottom of R-2 and were discharged at the top. This change was made to alleviate the difficulty of packing of solids observed during several carbon bed experiments. The revised reaction system is shown in Figure 21. The operating procedure for these experiments was the same as that followed for the carbon bed design experiments except that sintered granular A-100W, 1/8 inch-1/4 inch diameter boric oxide-carbon feed was charged to R-1. From experiment BL-125 on, the R_2/R_1 chlorine ratio was raised from 0.2 to 0.3 because it was noticed that some solids were passing through the carbon bed into the R-2 effluent gas lines. Results obtained from this series of experiments are summarized in Tables XIV and XV.

Preliminary plotting of boron trichloride production rates vs. total chlorine feed rates as measured by rotameter readings yielded highly scattered points for both spherical feed and briquetted feed experiments. Assuming that there were errors in the chlorine feed rates because of difficulties in maintaining constant flow throughout the experiments, the production rate vs. chlorine rate data were plotted with the use of the total recovery of chlorine plus Cl^- as a basis for the chlorine rate. Figure 22, Boron Trichloride Rate vs. Chlorine Rate, shows that very little scatter is evident and that spherical and briquetted feed exhibit identical production rates at given chlorine rates. This figure also shows that production rates are 15 per cent below theoretical. In other words, actual pass yields based on chlorine and Cl^- recovered were 85 per cent, the other 15 per cent chlorine was recovered in the form of hydrogen chloride, corrosion products, unconverted solids ($XB_2O_3 \cdot YBCl_3$) and free chlorine. The 85 per cent chlorine pass yield conversion based on chlorine and Cl^- recovered was substantially higher than the average value of 64 per cent obtained on the basis of rotameter readings.

C. **Reaction Characteristics of Powdered Feed**

The R-1 boric oxide-carbon feed for chlorination experiments with the use of a powdered charge was as follows

BL-77, A-100W briquets, pulverized, 6 to 30 mesh BL-78, A-100 granules, 30 mesh. Data from these two experiments a included in Tables XI, XII, and XIII.

The boron trichloride production rates for the powdered feed experiments compared favorably with those obtained for experiments with feed in the form of briquets, tablets, or spherical pellets. Boron pass yields were, however, very low. Inspection of the reactor bottoms showed evidence of severe channeling through the core and fusing of the bed. Therefore, the utilization of a fixed bed of boric-oxide-carbon powdered feed is not recommended.

VII. USE OF A COLD BED OF BORIC OXIDE-CARBON MATERIAL TO FILTER WHITE SOLIDS

It was belived that the necessity for a carbon bed "white solids" converter R-2 could be eliminated if the R-1 effluent gas stream were passed through a bed of cold boric oxide-carbon feed material which would condense the complex on the surfaces of the particles. The process would be readily adaptable to large scale production with a moving-bed counter current flow type reactor having a cold zone of boric oxide-carbon, briquets, at the uppermost part of the bed. These cold briquets would trap the solids which would be chlorinated along with the briquets when lowered into the hot reaction zone. Thirty bench scale chlorination experiments BL-146 to 172 and 193 to 201 were conducted to determine the feasibility of the process. The results are presented in Tables XVI, XVII, XVIII, and XIX.

The reaction system used for these experiments was the same as that used for the granular feed evaluation tests as illustrated in Figure 21. In the last 7 experiments, BL-193 to 201, a sodium hydroxide scrubber was put on stream in the recovery system to recover any chlorine not condensed in the refrigerated product condensers. The caustic scrubber was installed immediately upstream of the vent so that the Orsat analyses would include determination of carbon dioxide. The wet test meter measured carbon dioxide in addition to carbon monoxide, oxygen, and nitrogen.

With the exception of experiments BL-156 and 157, 11 inches of minus 1/4, plus 1/8-inch A-100W granules were charged to the 3-inch inside diamter primary chlorinator, R-1. For BL-157 and 156 the R . charge consisted of A-83W briquets which had served as the (R-2) white solids filtering medium (cold boric oxide-carbon bed experiments) for BL-154 and 155, respectively. In all experiments, the R-1 boric oxide-carbon charge was supported entirely in the hot zone of the gas fired reactor tube by carbon pellets. The material in the cold boric oxide-carbon bed (R-2) was A-150W briquets except for a few experiments in which carbon pellets were used. Twenty-four inches of material were charged to the R-2 solids filter for all experiments but BL-165, 167, 168 and 169, in which the bed was varied between

6 and 18 inches to determine the optimum size. In experiments BL-170, 171, and 172, the temperature of R-2 was varied to determine the maximum allowable temperature. Otherwise no heat was supplied to R-2. The last seven experiments of this series, BL-193 to 201 were conducted to determine the cause of low chlorine recoveries. Sampling techniques were improved during these latter experiments. In most cases, operating instructions called for passing chlorine to the primary chlorination for a predetermined period of time to theoretically react with the entire boron charge. A supplemental chlorine stream was not passed to R-2. Apart from the aforementioned changes, the operating procedure was the same as that followed for vertical carbon bed design experiments.

The data summarized in Table XIX show that the first set of chlorination experiments which utilized a 2-1/2 inside diameter x 24 inch long auxiliary bed of cold boric oxide-carbon briquets, experiments BL-148 to 155 exhibited slightly lower chlorine and boron pass yields than experiments incorporating a heated carbon bed with supplemental chlorine feed. This decrease in pass yields may be attributed to the fact that the R-1 effluent complex is retained in a cold boric oxide-carbon bed whereas they are converted to additional boron trichloride in a heated carbon bed. The average boron trichloride production rate for the cold, 24-inch boric oxide-carbon filter bed experiments, 2.08 lb./hr. was comparable to that obtained without use of an auxiliary bed. The effectiveness of the filtering action of the cold bed is shown by the high average value of 390 obtained for the ratio $B_{BCl_3}/B_{\text{white solids}}$. The value is considerably higher than the 8.3 value obtained for the regular experiments (direct chlorination of boric oxide-carbon briquets) and the 89 obtained for hot carbon bed experiments.

The high pass yields and overall yields obtained for BL-156 and 157 indicate that spent briquets coated with "white solids from the cold auxiliary boric oxide-carbon bed may be chlorinated without noticeable loss in yields. These data suggest that operation of a moving bed type reactor incorporating a layer of cold boric oxide-carbon feed material on top the heated reaction section may be feasible. Abnormally high boron recovery and yield data may be attributed to sampling errors.

Figure 23 shows the relation of height of cold bed to boron trichloride yields. Data from the following experiments are plotted: 24-inch bed, BL-166, 18-inch bed, BL-167, 12-inch bed, BL-168, 6-inch bed, BL-169. The sharp break in the boron pass yield curve between bed heights of 6 and 12 inches indicates that a 12-inch bed was required for maximum effectiveness at a chlorine rate of 15 cu.ft./hr. at S.T.P. This 12 x 2-1/2 inch diameter bed is equivalent to 0.02 ft.^{3} cold boric oxide-carbon briquets per lb. per hr. of boron trichloride produced. With a 6-inch bed filtration of the effluent gas stream for a chlorine rate of 15 cu. ft./hr. at S.T.P. was incomplete, and this resulted in plugging of glass wool solids trap. The decrease in pass yields for bed heights greater than 18 inches might have been caused by plugging tendencies resulting from increased packing of the bed. However it is more reasonable to suspect experimental error in as much as other experiments with a 24-inch cold boric oxide-carbon bed did not indicate any decrease in efficiency. The plot also shows that bed height had little effect on chlorine conversion which is to be expected because a cold bed merely traps out the solids and does not convert them.

Determination of the maximum temperature at which a filter bed of boric oxide-carbon briquets is effective was attempted in experiments BL-162 to 164 and 170 to 172. Bed temperatures were varied from 340 to 690°F. With the bed maintained at 500°F, there was evidence of "white solids" bridges between briquets as well as between briquets and filter tube walls. However, at temperatures above 600°F, the efficiency of the filter bed diminished rather significantly as evidenced by plugging of the glass wool traps. These tests show that, for maximum efficiency, the working part of the cold bed must be maintained at a temperature not exceeding 500°F. Figure 24 shows the relationship between filter bed temperatures and the $B_{BCl_3}/B_{white\ solids}$ ratio. This illustration emphasizes the importance of maintaining the working part of the filter bed at temperatures not exceeding 500°F and preferably at 400°F or less.

VIII. USE OF PREHEATED CHLORINE

Previous experimentation had indicated that, at certain temperatures, the heat of reaction might be sufficient to permit operation of the primary chlorinator without external heat. This hypothesis was made on the basis of heat balances and the fact that a considerable temperature increase of the bed was observed at start-up for bed temperatures of 1020 to approximately 1250°F. Twenty-nine bench scale chlorination experiments, BL-92 to 108RR were performed to investigate the degree of exothermicity. The results of these experiments are summarized in Tables XX and XXI.

A sketch of the reaction system utilized for this series of experiments is shown in Figure 25. The 24-inch x 3-inch bore split-element resistance wire furnace used to heat the carbon bed for previous experiments was utilized to preheat the chlorine. Initial preheating experiments showed that excessive heat losses occuring in the transfer line between the preheater and R-1 necessitated the heating of this section of pipe with resistance heaters. A carbon bed reactor was not included in the test apparatus.

The R-1 boric oxide-carbon charge consisted of 11 inches of A•83W briquets contained in the hot zone of the gas-fired reactor. Carbon pellets or briquets were charged to the chlorine preheater tube so as to attain good heat transfer from tube to gas. Except for several control experiments, the R-1 external gas heat was turned off simultaneously with the introduction of chlorine. During heat-up, a nitrogen purge rate equivalent in linear velocity to the chlorine velocity was maintained to distribute heat and to establish equilibrium conditions.

Initial attempts to chlorinate A•83W feed briquets with preheated chlorine were unsuccessful. These experiments were characterized by non-formation of boron trichloride, excessive hydrogen chloride formation, and the appearance of free chlorine in the effluent shortly after start-up. A series of 23 trouble-shooting experiments (TSR Runs) showed that the absence of reaction was caused by a combination of the following: (a) uneven temperature distribution throughout the reactor bed and improper location of the bed thermocouple combining to give misleading R-1 bed temperatures; (b) excessive hydrogen (water) content of the bed of pellets used to support the boric oxide-carbon briquet charge in R-1; and (c) a batch of inferior A•83W BOC briquets in R-1. The TSR results shown in Tables XX and XXI are for those experiments conducted after the operating difficulties were eliminated.

In Figure 26, time versus temperature curves for chlorination experiments with and without preheat of the chlorine and with and without maintenance of external heat to the primary reactor, R-1, are presented. The table included in Figure 26, summarizing the various operating conditions, also includes the volume of vent gas (carbon monoxide, carbon dioxide, and oxygen) per hour of operating time, indicating the relative amount of reaction that occurred for each experiment. Figure 26 shows that despite preheating of chlorine, a rapid fall in bed temperature occurred for experiments in which the primary reactor heat was off during chlorination. The rapid drop in bed temperature is reflected in much lower vent-gas volume per hour values and in much lower boron trichloride production rates and chlorine conversions. For example, TSR-20 (R-1 heat maintained) produced 6.84 $ft.^3$/hr. of vent gas whereas BL-106RR (R-1 heat off) yielded only 1.76 $ft.^3$/hr. The relatively high vent gas volume for BL-104 may be explained by the higher temperature of R-1 at the start.

From these data it is concluded that, without an external source of heat to the reactor, heat losses were too large for the heat of reaction to overcome. It is possible , however, that a more efficient preheater system combined with a better insulated reactor will yield more satisfactory results.

IX CHLORINATION OF ANHYDROUS BORAX-WITCO CARBON

Tests were conducted to determine the reactivity of anhydrous sodium tetraborate. The advantages of this material over boric oxide were assumed to be as follows: (a) sodium tetraborate is considerably cheaper than boric acid or boric oxide, (b) the melting point of sodium tetraborate is 1365°F as compared with 1110°F, the softening point of boric oxide (the melting point of sodium chloride would be formed as a by-product is 1472°F), (c) white solids might not be a problem. Accordingly, eighteen chlorination experiments were performed, and the results are summarized in Tables XXII, XXIII, XXIV, and XXV.

The apparatus used was the same as that described in Figure 21, consisting of a 3-inch inside diameter x 12-inch long nickel, gas-fired, primary reactor, R-1, and a 2-1/2 inch inside diameter x 24 inch long electrically (external) heated carbon bed. No changes were made in the recovery system except for the installation of a potassium iodide bubbler between the water scrubber and the wet test meter to recover free chlorine in the R-2 effluent which was not removed in the product condensers.

An 11-inch bed of sintered anhydrous borax Witco carbon pellets with 25 or 50 per cent excess carbon was charger to R-1. The excess carbon was determined from the stoichiometry of the reaction:

$$Na_2B_4O_7 + 7Cl_2 + 7C \longrightarrow 2NaCl + 4BCl_3 + 7CO \qquad (15)$$

Exceptions were (a) experiment BL-194 in which incompletely sintered material was purposely charged, and (b) experiments BL-209, 210, 216 and 217 in which the charge consisted of anhydrous borax chunks and Witco carbon 50 per cent excess pellets. The auxiliary carbon bed was charged with carbon briquets or pellets except as follows: (a) BL-173, 183-185, boric oxide-carbon briquets erroneously charged; (b) BL-194. A-100W granules, (cold filter bed). R-2 was heated to approximately 1400°F except in BL-194. The R-1 charge for experiments BL-186, 187 and 188 were heated to only 840°, 932°, and 752°F, respectively, to determine the reactivity at these low temperatures. Otherwise the R-1 charge was heated to between 1200 and 1600°F. Chlorine at 9.0 and 2.5 cu.ft./hr. at S.T.P. was fed to R-1 and R-2, respectively, except for BL-191 where a rate of 24.0 and 7.2 cu.ft./hr. at S.T.P. was utilized and for BL-194 in which the R-2 (cold boric oxide-carbon granules) chlorine feed was eliminated. In addition to the 9.0 cu.ft./hr. at S.T.P. chlorine feed, carbon monoxide at 1.0 cu.ft./hr. at S.T.P. was fed to R-1 for experiments BL-216 and 217, in an attempt to determine the effect of carbon monoxide addition on the heat balance and reactivity.

Table XXIV summarizes the yields, recoveries and production data for the various types of sodium tetraborate chlorination experiments. For comparison, average values are presented for experiments with boric oxide-carbon as the primary reactor charge.

Initial anhydrous borax chlorination experiments indicated that white solids were formed at essentially the same rate as for experiments with boric oxide-carbon feed. Temperature rise in the bed due to heat of reaction was observed to be 50 to 100 per cent greater for borax-carbon feed than for boric oxide-carbon feed. A significant increase in fusing of the reactor bottoms was also observed for borax-carbon experiments.

Experiments BL-186, 187 and 188 were performed at the low initial bed temperatures of 840, 932, and 752°F, respectively. Although the heat of reaction increased the bed temperature to as high as 1250°F for experiment BL-186, very little reaction occurred as evidenced by low pass yiel and boron trichloride production rates. Experiments BL-206 and 207 which were started at an initial bed temperature of 1290°F yielded 1.22 and 1.19 lb. boron trichloride/hr. (at 9.0 cu.ft./hr. at S.T.P. Cl_2 to R-1) whereas, experiments BL-204 and 208 with an initial bed temperature of 1100°F, produced only 0.82 and 0.74 lb. boron trichloride/hr. respectively. Under similar conditions the chlorination of boric oxide-carbon feed yielded 1.41 lb. boron trichloride/hr. These data indicate that reaction can be initiated at a solids temperature of approximately 1100°F but that higher temperatures favor increased boron trichloride production rates.

A comparison of recoveries, yields and production rates for experiments using boric oxide-carbon feed with those using borax-carbon feed (experiments BL-204, 206, 207, 208) shows that production rates were 40 to 50 per cent lower with use of the borax-carbon. The hydrogen chloride-boron trichloride weight ratio average for the borax-carbon chlorination experiments was slightly higher than the 0.157 value for boric oxide-carbon experiments. The use of a heated carbon bed was equally effective in eliminating white solids in the effluent gas lines.

Table XXIV also shows that for experiments BL-187 and 188 which were started at very low temperatures, in addition to the low production rate and pass yields, hydrogen chloride-boron trichloride ratios were extremely high. This is presumably due to the reaction of the meager amounts of boron trichloride produced with water in the borax-carbon feed to form hydrogen chloride and boric oxide or boric acid.

For experiments with a chlorine rate of 9.0 cu.ft./hr. at S.T.P. to R-1 (and 2.5 cu.ft./hr. to R-2) the amount of sodium recovered in R-2 as chloride or possibly as borate did not exceed 2 per cent of the sodium-charged to R-1. In experiment BL-191 the chlorine feed rate was increased to 24 cu.ft./hr. to determine whether it would be accompanied by a corresponding increase in the amount of sodium carried over to R-2. No increase was noted. Experiment BL-184 shows that the carbon monoxide-carbon dioxide ratio increased from 0.60 to 2.5 as the experiment progressed. This increase is probably attributed to the increase in carbon bed temperature from 1385 to 1598°F. The charge for BL-194 consisted of incompletely sintered borax-carbon pellets. During this experiment, frequent plugging of the filter trap and condensers was observed. The boron pass yield, 18 per cent, and boron trichloride production rate, 0.72 lb./hr., were much lower than the averages for experiments BL-204, 206, 207, and 208, which were 48.9 per cent and 0.99 lb. boron trichloride/hr.

Material balance calculations for BL-174 showed that 70 per cent of the sodium in the borax-carbon charge was converted to sodium chloride, but that only 26 per cent of the boron content was reacted and recovered as product. In all experiments, the amount of sodium chloride formed as determined by chloride ion analysis of the reactor bottoms (ash or residue) was considerably in excess of stoichiometry for that which could be formed via the equation

$$2Na_2B_4O_7 + 14Cl_2 + 7C \longrightarrow 4NaCl + 8BCl_3 + 7CO_2 \qquad (3)$$

Experiments BL-204 to 208 were conducted with 25 per cent excess carbon in borax-carbon pellets to determine whether any conclusions could be reached regarding preferential chlorination of sodium over boron. It will be recalled that the average boron and chlorine pass yields and boron trichloride production rates for these experiments were approximately 60 to 70 per cent of those for experiments with boric oxide-carbon briquets as primary reactor charge. On the basis of the foregoing reaction, the chlorine pass yield and boron trichloride production rate for borax feed should be 85.7 per cent of that for boric oxide-carbon feed. The discrepancy suggests that the reaction may be proceeding by a different path. A plausible explanation is offered by the following equations:

$$2Na_2B_4O_7 + 14Cl_2 + 7C \longrightarrow 4NaCl + 8BCl_3 + 7CO_2 \qquad (3)$$

$$3Na_2B_4O_7 + 2BCl_3 \longrightarrow 7B_2O_3 + 6NaCl \qquad (17)$$

$$2B_2O_3 + 3C + 6Cl_2 \longrightarrow 4BCl_3 + 3CO_2 \qquad (1)$$

$$CO_2 + C \rightleftharpoons 2CO \qquad (2)$$

If in addition to reaction (3), reactions (17) and (1) occur, but (1) is incomplete, excessive sodium chloride is formed and lower boron trichloride production rates are obtained. Furthermore, the "white solids" observed with use of borax-carbon feed can be explained by reactions (17) and (1). The severe fusion of the reactor bottoms characteristic of borax-carbon experiments cannot be explained on the basis of reaction (3) and the relative melting (softening) points of borax, sodium chloride, and boric oxide, which are 1365°, 1472° and 1110°F respectively. However, the occurrence of reaction (17) conveniently accounts for the phenomenon.

Table XXV shows that the calculated R-2 effluent gas stream composition for borax-carbon feed, experiment BL-207, compares favorably with that for boric oxide-carbon briquet feed, experiment BL-141.

In experiments BL-209 and 210 the reactor charge consisted of chunks of anhydrous borax (up to 1/2 inch) interspersed with carbon pellets to give an approximate overall feed formulation of NBO.50W., or 50 per cent excess Witco carbon. Data show that virtually no product was obtained and that the boron and chlorine pass yields were extremely low. However, in experiment BL-210, 152 g. of hydrogen chloride, representing about 15 per cent of the chlorine charged, was recovered in the water scrubber indicating that some boron trichloride had been formed and then hydrolyzed, or that the residual hydrogen (as water) had formed hydrogen chloride in accordance with the following equations

$$H_2O + C \longrightarrow CO + H_2 \tag{18}$$

and

$$H_2 + Cl_2 \longrightarrow 2HCl \tag{19}$$

The R-1 charge for experiments BL-216 and 217 was the same as that for BL-209 and 210. In addition to chlorine at 9.0, carbon monoxide at 1.0 cu.ft./hr. at S.T.P. was passed to the primary chlorinator. Results show that only insignificant amounts of boron trichloride were formed.

X. CHLORINATION OF BORON CARBIDE

Seventeen batch experiments were performed to evaluate the reaction characteristics of boron carbide. In addition to its higher heat of reaction, other possible advantages from use of boron carbide as the source of boron include (a) the elimination of fusing due to the high melting point of boron carbide (4260°F), and (b) elimination of white solids due to the absence of boric oxide. Operating conditions and production data for the tests are summarized in Tables XXVI, XXVII, and XXVIII. Average results for boric oxide-carbon experiments are included in Table XXVIII for comparison.

The apparatus used for these evaluation experiments was the same as that used for the spherical boric oxide-carbon feed and borax feed experiments and is illustrated in Figure 21. A caustic scrubber was added for a few of the final tests.

The R-1 charge consisted of (a) 1/4 to 1/2 inch diameter boron carbide chunks mixed with carbon pellets in varying proportions (experiments BL-158 to 182); or (b) powdered boron carbide and Witco carbon, (BL-189 and -190); or (c) A-100W pellets containing 0.05 lbs. boron carbide for each pound of boron carbide plus boric acid (BL-213, 214, and 215); or (d) same as (c) but in spherical pellet form and with a boron carbide/boron carbide plus boric acid ratio of 0.0123, (BL-222) For all experiments, the R-1 charge was supported in the hot zone by a bed of carbon pellets. With the exception of BL-158 and 159, the gas heat source to R-1 was turned off simultaneously with the introduction of chlorine. In experiments BL-158 to 161, -189 and -190 a secondary reactor R-2, was not used. A vertical carbon bed contained in a 2-1/2 inch inside diameter x 24 inch heated pipe to which supplemental chlorine was fed, was used for experiments BL-175, 176, 177, 179 and 213-215 whereas a cold bed of boric oxide-carbon briquets was used for experiments BL-180, 181, 182 and 222. Chlorine was passed to R-1 at a constant rate, except for BL-176 to 181 where the rate was varied in an attempt to sustain the reaction without supplying additional heat.

Operating instructions called for shutdown when (a) the bed appeared to be exhausted as evidenced by free chlorine in the effluent, or (b) when the R-1 bed temperature had dropped sufficiently so as to no longer sustain reaction, or (c) operating difficulties necessitated shutdown. A primary reactor charge of 100 per cent boron carbide was not tested due to the known excessive heat of reaction.

The first two boron carbide chlorination experiments BL-158 and 159, which utilized an R-1 charge of boron carbide chunks (17 per cent) and 1/4-inch diameter carbon pellets (83 per cent) at a start up temperature of 1290°F had to be terminated prematurely because of excessive leakage caused by the attainment of excessively high temperatures (above 1800°F). Yields were low for the same reason. Table XXVIII shows a significant increase in the $B_{BCl_3}/B_{\text{white solids}}$ ratio, 148. vs 8.5 for boric oxide-carbon briquets) which confirms the hypothesis that boric oxide must be present to form "white solids". The rather high hydrogen chloride-boron trichloride weight ratio is the result of excessive hydrogen as water in the carbon pellets and/or the short duration of the two experiments. Experiments of short duration usually exhibit high hydrogen chloride-boron trichloride ratios because boron trichloride formed will initially react with any water present to form boric oxide and hydrogen chloride until the water content of the charge has been exhausted. In chlorination experiments BL-160 and 161 (same charge and chlorine rate as 158 and 159) the external gas heat supply to R-1 was turned off simultaneously with the introduction of chlorine to see whether the heat of reaction was sufficient to balance heat losses and thus sustain reaction. A temperature rise of approximately 30°F (to 1320°F) occurred shortly after start-up with chlorine after which the temperature of the bed dropped rapidly and reached 1020°F, 40 minutes after going on stream. The rapid reduction in bed temperature and consequent loss of reaction was reflected in (a) low chlorine pass yields, 26 per cent; (b) low production rates, 0.45 lb. boron trichloride, and (c) high chlorine content of the condensed product, 66. per cent.

Attempts to sustain reaction over a period of time by varying the boron carbide concentration of the charge and by regulating the chlorine feed rate throughout the experiment (BL-175 to 183), were partially successful. Figure 27 depicts the time-temperature curves for two of the experiments, BL-179 and 181, and for an experiment with boric oxide-carbon briquents. Although BL-179 and 181 were started at essentially the same temperature, 1100°F and at the same initial chlorine rate 9.0 cu. ft./hr. at S.T.P. to R-1 and 1.0 to R-2 and had approximately the same boron carbide concentration, reaction temperatures were maintained successfully in BL-179 whereas a rapid drop off was observed for BL-181. Higher pass yields and production rates were obtained in BL-179. Boron and chlorine pass yields for BL-179 compare favorably with the average values obtained with use of boric oxide-carbon briquets and no carbon bed. However, production rates were slightly lower.

It was thought that the generally low chlorine and boron pass yields experienced for numerous boron carbide chlorination experiments were caused by poor distribution of boron throughout the reactor charge. Futhermore, the poor temperature distribution experienced in these experiments, (hot spots), was also thought to have been the result of poor boron distribution. Accordingly, BL-189 and 190 were performed with a charge of intimately mixed 20 to 200 mesh boron carbide (27 per cent) and 20 to 40 mesh Witco carbon (73 per cent). The Witco carbon was dried at 500°F before mixing with the boron carbide powder. A carbon bed was not used for these two experiments. Excessive heat of reaction resulted in burning of the R-1 thermowell and premature shutdown. Table XXVIII shows low boron pass yields for these tests. However the chlorine conversion of 77 per cent and boron trichloride production rate of 1.53 lb./hr. for experiment BL-190 are superior to corresponding boric oxide-carbon briquet, -no carbon bed averages. The most significant result obtained in experiment BL-190 was the low hydrogen chloride-boron trichloride weight ratio (0.026). In all previous experiments the carbon in the bed consisted of sintered Witco pellets which contain hydrogen equivalent to between 1 and 3 per cent water originating primarily from water added during the pellet preparation process. However, in experiment BL-190, water was never added to the carbon.

Examination of the residue in these experiments failed to indicate any fusing or softening. The residues were free-flowing. Furthermore, the amount of "white solids" deposited in the overhead lines was negligible.

In experiments BL-213, 214, and 215, the R-1 charge consisted of 1/4-inch tablets prepared from mixtures of boric oxide, boron carbide, and carbon formulated to 100 per cent excess carbon. This charge was formulated to yield a boron carbide-boric acid plus boron carbide ratio of 1/20. At R-1 chlorine rates of 15 and 13 cu.ft./hr. at S.T.P. for BL-213 and 214 respectively, reaction was excellent. The reaction was sustained for 30 minutes (R-1 heat off during experiment), until excessive heat necessitated shutdown. The production data for experiment BL-213 presented in Table XXV show that reactivity of this feed compared favorably with that of boric oxide-carbon briquets maintained in a continuously heated reactor tube. In experiment BL-215, the R-1 chlorine rate was reduced to 9.0 cu.ft./hr. at S.T.P. Reaction temperatures could not be sustained at this lower chlorine rate. After a 100°F temperature rise to 1310°F, the bed temperature dropped to 1000°F rapidly. Experiment BL-222 (A·100W + B_4C feed, $B_4C/B_4C + H_3BO_3 = 0.0123$) had to be discontinued after 13 minutes of chlorinating time because of plugs caused by deposition of solids in the line. The hydrogen content of the feed was 1.02 per cent.

XI. USE OF CHLORINE-OXYGEN MIXTURES CHLORINATION OF BORIC OXIDE - CARBON FEED WITH A MIXTURE OF CHLORINE AND OXYGEN

In experiments BL-218, 219, and 221, the chlorine feed to R-1 was supplemented with oxygen to determine whether additional heat could be obtained through combustion of the excess carbon present in the solids charge. Data from these experiments are contained in Tables XXIX and XXX.

The batch type reactor system described in Figure 21 was utilized. No changes were made in the recovery system.

A 3-inch diameter x 11-inch bed of 1/8-1/4-inch diameter A·100W granules was charged to R-1. A·150W briquets were charged to R-2 to serve as a white solids filter. The R-1 bed was heated to 1250°F and the external source of reactor heat, gas, was turned off with introduction of the mixture of chlorine and oxygen. Each experiment was on stream for 1.0 hour, at which time the experiment was purposely terminated.

Time-temperature curves for the three experiments shown in Figure 28 indicate that considerable additional heat was obtained. Conversions and boron trichloride production rates were substantially better than for experiments in which no oxygen was fed but considerably lower than for experiments in which external heat was maintained throughout the experiment.

XII. ROTARY TUBE CHLORINATION

As part of a general program to investigate various other methods of producing boron trichloride, a series of bench scale chlorination experiments were performed with a rotary kiln type reactor. The results of six experiments are summarized in Tables XXXI and XXXII.

Figure 29 is an illustration of the Rotary Chlorinator. The reactor was a modified Bartlett-Snow Rotary Calciner consisting essentially of a 7-foot long nickel alloy tube with a 5-1/2-inch inside diameter carbon liner. Heat was supplied by a gas furnace which heated 2-3/4 feet of the retort tube. Four 3/4-inch flights, each 3-1/2 feet long, were inserted in the furnace chamber. Dried and preheated chlorine was fed counter current to the flow of solids. The boric oxide-carbon feed was charged by a screw type feeder. The recovery system was essentially the same as illustrated in Figures 1 and 2.

The operating procedure was as follows:

(a) Start retort rotating
(b) Preheat the retort for 2 to 3 hours
(c) Charge feed hopper and feed boric oxide-carbon granules (or powder) for 2 hours to build up a bed
(d) Pass chlorine into the system

The chlorine rate during experiments RC-4, 5 and 6 was varied to establish production rate versus chlorine rate relationships.

In experiment RC-1, the temperature in the reaction zone was determined by a thermocouple inserted into the bed of rotating feed. However, after this experiment, flights were installed and the temperature was estimated by visual observation of the degree of glow on the retort tube. In experiments RC-4, 5 and 6, the effluent gas stream was passed through a glass wool filter and then directly to auxiliary water and caustic scrubbers until the effluent was dry. The foregoing modification was effected to reduce plugging which plagued earlier experiments.

As shown in Table XXXI, the first 3 experiments were performed with sintered granules as the feed material. Powdered feed for RC-4, 5 and 6 was prepared by pulverizing granules and then drying the powder at 500°F for 3 hours. The feed analysis for all experiments was approximately the same.

For the first three experiments, it was necessary to operate the chlorinator with the retort tube revolving at the lowest speed because both the retort tube and the solids feed screw were connected to the same drive. Even at the lowest speed the amount of solids fed was 5 times the stoichiometric quantity required to react with the chlorine. The chlorine feed rate was limited by the capacity of the recovery system. Table XXXII (recoveries and yields) shows that very little product was formed. Chlorine recovery was low because of leaks in the system. Frequent shutdown of experiments RC-1 to 3 was necessitated by the formation of plugs in the effluent gas lines and in the recovery system. It is believed that almost all of the boron trichloride which was formed reacted with the water contained in the excess boric oxide-carbon granular feed to form hydrogen chloride, boric oxide and boric acid solids which plugged the effluent gas lines. For experiments RC-4, 5 and 6, the solids feeder was connected to a separate drive which permitted a slower solids feed rate and reduced the amount of water introduced with the feed. At the same time it permitted a more rapid rotation of the retort tube which improved the flight action.

During a calibration experiment with powdered feed, good flight action was observed in the retort tube. The cylinder loading was about 4-per cent of the cylinder volume.

For experiments RC-4, 5 and 6 a line out period described in the operating procedure was instituted. However, during experiment RC-4, only one water scrubber was used. The highest boron trichloride production rate, 1.0 lb./hr./ft.^{2} of cross sectional area was obtained in FC-6, with a chlorine conversion of 34.7 per cent, and a chlorine recovery of 71.8 per cent. This production rate is based on the experiment time only and excludes the line out period. The item "HCl Production Rate as BCl_3" in Table XXXII is the amount of boron trichloride that reacted with water in the feed, to form hydrogen chloride.

Figure 30 shows the production rate of boron trichloride, the production rate of boron trichloride plus hydrogen chloride as boron trichloride and the chlorine conversion as a function of the chloride feed rate for experiments RC-4, 5-1, 5-2, and 6. The theroetical production rate of boron trichloride, 100 per cent chlorine conversion, based on chlorine fed is also shown for purposes of comparison. These data show that a maximum production rate and chlorine conversion was attained at a chlorine rate intermediate in the test range. The phenomenon may be attributed to the cooling effect of chlorine when fed at rates exceeding 13.5 cu.ft./hr. at S.T.P. The bed temperature may have dropped below the minimum, about 1100°F required for reaction. However, other factors such as degree of leakage and feed characteristics may have influenced the shape of the production rate and conversion curves.

The purpose of the Rotary Chlorination experiments was not to obtain extensive operating data but to determine the feasibility of the process. Results obtained from six experiments have shown that boron trichloride can be produced in limited yields by chlorination of boric oxide-carbon feed material in a Rotary-Calciner type reactor. However process variables such as flight design, residence time of feed, effect of chlorine rate over a wider range, effect of feed characteristics such as particle size and per cent excess carbon, would have to be investigated before building a pilot plant reactor. Based on operating experience, it is anticipated that fusing of boric oxide-carbon feed on the retort walls and in the retort bed would present obstacles to continuous chlorination.

XIII. CONCLUSIONS

A. Externally heated reactors, either electrically or gas heated were found to give better control of bed temperatures than an internally heated resistance bed electrode furnace in the chlorination of mixtures of boric oxide and carbon at elevated temperatures. Heating experiments with use of a resistance bed-electrode furnace were accompanied by (a) preferential current paths causing localized heating and poor temperature distribution across the bed, (b) frequent loss of contact between the electrodes and the bed and (c) fusing of the bed.

B. Powdered mixtures of boric oxide and carbon could not be chlorinated satisfactorily in a fixed bed due to channeling of chlorine caused by fusion of the bed at temperatures required for reaction. Feed formulations containing 100 per cent excess carbon were tested.

C. Tabletted mixtures of boric oxide and furnace black carbon containing 100 per cent excess carbon were chlorinated satisfactorily at 1100 to 1500°F without fusion of the reactor bed.

D. Boric oxide-carbon feed in the form of almond shaped briquets or 1/8- to 1/4-inch spherical granules chlorinated as well as tabletted feed.

E. An increase in the excess carbon content from 50 to 300 per cent was accompanied by a decrease in the boron trichloride production rate, and chlorine conversion. Apparently, this was caused by decreased boron concentrations of the reactor bed.

F. Increasing the reactor bed temperature from 1125 to at least 1350°F resulted in an increase in the chlorine conversion from 50 to 82 per cent.

G. Vent gas analysis for experiments in which the bed height was varied from 3 to 12 inches indicated that carbon dioxide rather than carbon monoxide is formed first.

H. A chlorine residence time of approximately 0.25 seconds is required to produce a product free of chlorine.

I. The following results were obtained for chlorinating a 12-inch deep x 3-inch diameter bed of boric oxide-carbon briquets at approximately 1300°F, and at a chlorine rate of 15 cu.ft./hr. at S.T.P.

BORON			CHLORINE		Condensed Product Impurities		BCl_3 Production Rate lb./hr.	$\frac{B_{BCl_3}}{B_{solids}}$	$\frac{HCl}{BCl_3}$
Pass Yield per cent	Over-all per cent	Recovery per cent	Pass Yield per cent	Recovery per cent	Cl_2 per cent	$COCl_2$ per cent			
44	72	78	62	83	6.0 to 27	0.0 to 0.9	2.07	8.5	0.11

J. The formation of hydrogen chloride by the reaction of water contained in the boric oxide-carbon feed, with boron trichloride was minimized by observing rigid sintering and feed storage procedures.

K. "White solids" which were formed as a by-product and deposited in the effluent gas lines, was virtually eliminated by passing the primary reactor effluent through a secondary reactor containing hot carbon pellets and having a separate chlorine feed. A bed containing 0.012 $ft.^3$ of carbon per pound per hour of boron trichloride produced, and heated to approximately 1400°F, was required to convert the "white solids" to additional boron trichloride.

L. An unheated filter bed of 0.02 boric oxide-carbon briquets/pound/hour of boron trichloride produced was also found to be effective in eliminating the problem of "white solids".

M. Boric oxide-carbon chlorination experiments with preheated chlorine were inconclusive because of the inadequacy of the test equipment.

N. The inclusion of small amounts of boron carbide in the boric oxide-carbon charge provides sufficient additional heat when reacted with chlorine to maintain reaction temperature without external heat.

O. Supplementing the chlorine feed gas with oxygen resulted in additional heat but not enough to sustain the reaction.

P. Chlorination of sodium tetraborate plus carbon is characterized by: (a) preferential chlorination of sodium; (b) excessive fusion of the reactor bottoms; (c) "white solids" formation at approximately the same rate as with boric oxide-carbon feed. The excessive fusion of the bottoms is believed to be caused by the formation of boric oxide as an intermediate. The preparation of boron trichloride by the chlorination of borax-carbon in a fixed bed reactor is not recommended.

Q. Chlorination experiments in a rotary kiln type reactor with boric oxide-carbon granules as solid feed showed that boron trichloride could be produced in limited yields but that operation of a commercial size reactor is not feasible because of the low chlorine conversion.

XIV. ATTACHMENTS

Tables I through XXXII inclusive

Figures 1 through 30 inclusive

TABLE I
RAW MATERIALS

A. CARBON, WITCO CHEMICAL COMPANY: CHEMICAL AND PHYSICAL DATA

	Bench Scale Stock (a)	Pilot Plant Stock (b)
Fixed Carbon (per cent)	99	99
Moisture (max. per cent)	4 (typical 1)	4
Ash (per cent)	0.2	?
Particle Size ($m\mu$)	70	70
Specific Gravity	1.90	1.80
Density (apparent lb./cu.ft.)	20	27-30

(a) SRF-F-1 Witco powder
(b) SRF beads, approximately 1/16 inch diameter.

B. BORIC OXIDE, BORIC ACID, AND ANHYDROUS BORAX: CHEMICAL AND PHYSICAL DATA

	B_2O_3 (a)(b)	H_3BO_3(a)(b)	$Na_2B_4O_7$ (a)(c)
B_2O_3 (per cent)	98.83	56.3(theoretical)	69.2(theoretical)
H_2O (per cent)	0.75	43.7(theoretical)	Na_2O 30.8 (theoretical)
Na (per cent, maximum-typical)	0.1-0.05	0.1-0.005	
SiO_2(per cent, maximum-typical)	0.3-0.14	0.3-0.14	0.05-0.015
Al_2O_3(per cent, maximum-typical)	0.2-0.09	0.2-0.09	0.05-0.007
Fe_2O_3(per cent, maximum-typical)	0.1-0.04	0.1-0.04	0.01-0.005
CaO(per cent, maximum-typical)	0.05-none	0.05-none	0.02-none
MgO(per cent, maximum-typical)	0.02-none	0.02-none	0.01-none
Bulk Density (lb./cu.ft.) (loose packed) 60 mesh	6.0		SO_3 0.27-0.005 Typical Analysis $Na_2B_4O_7$-99.3 per cent
100 mesh	61.5		H_2O 0.4 per cent

(a) U.S. Borax and Chemical Corporation

(b) 60 and 100 mesh technical grade powder

(c) Dust

TABLE I (Continued)
RAW MATERIALS

C. BORON CARBIDE CHEMICAL AND PHYSICAL DATA

	CIR (a)	Norbide (b) Lot 1	Lot 2	Lot 3
B_4C (per cent)	70.9	91.2	82.4	77.6
Residual (c) per cent (free carbon, ash, water)	29.1	8.5	15.1	18.6
B_2O_3 (per cent)	not given	0.3	2.5	4.8
Acid Insoluble	not given	98.9	96.6	94.4
Particle Size	not given	30 mesh to 1/4 in.	3/16 to 1/2 in.	3/16 to 1/2 in.

(a) Cleveland Industrial Research, (technical grade). This feed was used in experiments BL-158 to 161.
(b) Norton Company, technical grade.
(c) Determined by difference.

D. CHLORINE, HOOKER ELECTROCHEMICAL COMPANY, 100 POUND CYLINDERS

Impurities	
Carbon Tetrachloride	- 40 parts per million
Chloroform	- 40 parts per million
Hexachlorethane	- 25 parts per million
Ferric Chloride	- 25 parts per million
Carbon Dioxide	- 0.5 per cent by volume
Oxygen	- 0.4 per cent by volume
Nitrogen	- 0.07 per cent by volume

E. NITROGEN, AIR REDUCTION COMPANY

Oil pump grade, in cylinders of 224 cubic feet at standard temperature and pressure.

TABLE II
HEATING CHARACTERISTICS OF ELECTRODE FURNACE I

Experiment Number	Duration of Experiment hr.	Maximum Power Watts	Maximum Temperature °F	Power to Maintain Temperature	Remarks
450D-20A	1	1200	1593	-	Current paths erratic. Finally stopped. Bed fused.
450D-20B	1	850	636	-	Current paths erratic. Finally stopped. Bed fused.
450D-20C	1/2	800	492	-	Fuses failed in all three circuits.
450D-20D	1	850	573	-	Fuses failed in all three circuits. Bed fused.
450D-22	-	-	652	-	Measured resistances through various paths. Ranged from 20-900 ohms.
450D-24	1	560	499	-	Poor control and heating.
450D-26A	3 1/2	700	1618	130W at 862°F	Checked heat distribution, used two circuits.
450D-26B	2 1/2	360	1077	110W at 951°F	Checked heat distribution, used two circuits.
450D-26C	8	166	1061	140W at 998°F	Checked heat distribution, used two circuits.
450D-29	7	430	688	360W at 645°F	Poor control and heating.

TABLE III

HEATING CHARACTERISTICS, ELECTRODE FURNACE II, CHARGED WITH CARBON PELLETS (a)

Time min.	Temperature No. I °F (b)	Temperature No. II °F (b)	Temperature No. III °F (b)	Volts (c)	Amperes (c)	Power Watts
0	158	158	158	0	0	0
40	518	583	613	19	18	592
60	734	883	1012	23	19	757
90	1274	1137	1022	23	19	757
100	1274	1176	1174	24	20	832
170	1238	1203	1130	24	17	706
After	1302	1745	1374	24	23	956

(a) Equilibrium at 1300°F
Furnace purged with nitrogen at 1 cu.ft./hr. S.T.P.

(b) Thermocouples spaced 2 1/2" apart - No. I, top thermocouple

(c) Voltage and amperage readings are the average readings of three electrodes.

TABLE IV

OPERATING CONDITIONS FOR CHLORINATION EXPERIMENTS

(PRELIMINARY PROCESS DEVELOPMENT STUDIES WITH RESISTANCE WRAPPED REACTOR)

Expt. No.	Cl_2 Rate cu.ft./hr. at S.T.P.	Solid Feed Formulation	Bed Height (R-1) in.	Bed Temperature (R-1) °F	Duration of Expt. hr.	Time Before Plug hr.	Remarks (a)
450D-41	2.6	A-100W-15-K-150	12.	1328	3.875	3.875	
450D-43	4.0	A-100W-15-K-150	12	1360	3.160	1.920	
450D-45	3.6	A-100W-15-K-150	12	1320	3.33	1.87	Effluent gas line plug. Frequent shutdowns.
450D-46	3.6	A-100W-15-K-150	12	1310	3.16	1.5	Excess chlorine 160 min. Line plug. 801 g. pellets added during experiment.
450D-47	1.7	A-100W-15-K-150	12	1310	5.25	3.33	Excess chlorine 190 min. Plug in throat of header. 705 g. feed added during experiment.
450D-48	5.2	A-100W-15-K-150	12	1350	2.5	0.83	
BL-1	6.8	A-100W-15-K-150	12	1302	1.75	1.17	Excess chlorine 45 min. 1210g. feed added during experiment.
BL-2	8.3	A-100W-15-K-150	12	1358	0.97	0.5	Excess chlorine 20 min. Frequent shutdowns due to plugs.
BL-3	3.4	0-20W-20-K-150	12	1310	3.3	1.63	Excess chlorine 65 min. 938 g. feed added during experiment shutdown, hole in thermowell.
BL-4	6.8	0-20W-20-K-150	12	1332	0.85	0.85	368 g. feed added during experiment. Shutdown due to severe leaks.
BL-5	8.3	0-20W-20-K-150	12	1350	1.26	0.88	Excess chlorine 12 min. 881 g. feed added during experiment. Frequent shutdown, vent line plug.
BL-6	0.9	0-20W-20-K-150	12	1322	5.7	1.73	Excess chlorine 104 min. Frequent shutdown due to leaks. Ran continuously for 238 min.

TABLE IV (Continued)
OPERATING CONDITIONS FOR CHLORINATION EXPERIMENTS
(PRELIMINARY PROCESS DEVELOPMENT STUDIES WITH RESISTANCE WRAPPED REACTOR) (Continued)

Expt. No.	Cl_2 Rate cu.ft./hr. at S.T.P.	Solid Feed Formulation	Bed Height (R-1) in.	Bed Temperature (R-1) °F	Duration of Expt. hr.	Time Before Plug hr.	Remarks (a)
BL-7	6.8	0-20W-20-K-150	12	1310	1.3	0.25	Four inch reactor. 286 g. feed added during experiment. Frequent shutdown due to plugs in effluent gas line.
BL-8	3.6	0-200W-30-K-150	12	1364	1.66	1.0	Excess chlorine 90 min. 500 g. feed added during experiment. Frequent shutdown due to plugs.
BL-9	6.8	0-200W-25-K-150	12	1323	1.5	0.78	Excess chlorine 28 min. 1255 g. feed added during experiment. Frequent shutdown due to plugs and leaks in effluent line.
BL-10	9.5	0-200W-25-K-150	12	1324	0.97	0.22	943 g. feed added during experiment 4 plugs: line, furnace feed line, line, scrubber. Frequent shutdown.
BL-11	3.6	0-200W-25-K-150	12	1593	1.03	1.03	165 g. feed added during experiment. Plug in neck.
BL-12	11.0	0-200W-25-K-150	12	1307	0.72	0.33	No excess chlorine at 34 cu.ft./hr. S.T.P. after 11 min. Frequent shutdown due to plug in effluent gas lines.
BL-13	9.1	0-100W-25-K-150	12	1323	1.10	0.35	1679 g. feed added during experiment. Frequent shutdown due to line plug.
BL-14	8.8	0-200W-25-K-150	3 3/8	1280	0.166	0.17	Excess chlorine 2 min. 120 g. feed added during experiment. Plugged lines.
BL-15	8.8	0-200W-25-K-150	2 1/8	1346	0.454	0.35	317 g. feed added during experiment. Frequent shutdown due to plugged lines.

TABLE IV (Continued)

OPERATING CONDITIONS FOR CHLORINATION EXPERIMENTS

(PRELIMINARY PROCESS DEVELOPMENT STUDIES WITH RESISTANCE WRAPPED REACTOR) (Continued)

Expt. No.	Cl_2 Rate cu.ft./hr. at S.T.P.	Solid Feed Formulation	Bed Height (R-1) in.	Bed Temperature (R-1) °F	Duration of Expt. hr.	Time Before Plug hr.	Remarks
BL-16	3.6	0-100W-25-K-150	12	1154	1.5	1.17	495 g. feed added during experiment. Frequent shutdown due to plug and bed plug.
BL-17	7.6	0-100W-25-K-150	12	1124	0.97	0.33	Excess chlorine 46 min. Frequent shutdown due to plugs in bed.
BL-18	3.2	0-100W-25-K-150	12	1084	1.33	1.33	Falling pellet experiment 35 g./5 min. fed and removed from bottom plugs.
BL-19	34.0	0-100W-25-K-150	12	1302	0.28	0.133	50 g. feed added during experiment. Frequent shutdown due to plugs.
BL-20	11.5	0-100W-25-K-150	6	1082	0.35	No Plug	178 g. feed added during experiment. Shutdown due to temperature drop in bed.
BL-21	11.5	0-100W-25-K-150	6	1319	0.85	0.16	520 g. feed added during experiment. Frequent shutdown due to effluent gas line plugs.
BL-22	17.8 average	0-200W-25-K-150	12	1174	0.95	0.18	80 g. feed added during experiment. Frequent shutdown due to effluent gas line plugs.
BL-23	11.5	0-200W-25-K-150	6	1130	0.45	0.13	Frequent shutdown due to 3 line plugs and a filter plug.
BL-24	3.6	0-100W-25-K-150	12	1242	0.57	No Plug	740 g. feed added during experiment. Powder feed.
BL-25	11.5	0-200W-25-K-150	6	1341	0.77	0.32	Frequent shutdown due to effluent gas line plug.
BL-26	34.	0-100W-25-K-150	12	1180	0.48	0.11	Excess chlorine 9 min. Frequent shutdown due to effluent gas line plugs.

TABLE IV (Continued)

OPERATING CONDITIONS FOR CHLORINATION EXPERIMENTS

(PRELIMINARY PROCESS DEVELOPMENT STUDIES WITH RESISTANCE WRAPPED REACTOR) (Continued)

Expt. No.	Cl_2 Rate cu.ft./hr. at S.T.P.	Solid Feed Formulation	Bed Height (R-1) in.	Bed Temperature (R-1) °F	Duration of Expt. hr.	Time Before Plug hr.	Remarks
BL-27	11.5	0-100W-25-K-150	6	1591	0.42	0.42	Short circuit in heater.
BL-28	3.6-5.0	0-100W-25-K-150	12	1292	0.80	0.35	Pre-heated falling pellet. Frequent shutdown due to line plugs and leaks.
BL-29	9.0	0-100W-25-K-150	3	1292	0.38	0.20	350 . feed added in 70 g. increments during experiment. Frequent shutdown due to line plugs.
BL-30	9.0	0-100W-25-K-150	3	1112	1.23	0.72	560 g. feed added in 70 and 140 g. increments.
BL-31	9.0	0-100W-25-K-150	3	1472	1.17	No Plug	490 g. feed added during experiment. Frequent shutdown due to effluent gas line plugs.
BL-32	9.0	0-100W-25-K-150	3	1112	1.00	No Plug	376 g. feed added during experiment.
BL-33	12.5	0-100W-25-K-150	3	1472	0.37	No Plug	Excess chlorine 22 min. 280 g. feed added during experiment.

(a) Pellets used as reactor charge except where noted. 3 inch NPS nickel reactor used except where noted.

TABLE V
RESULTS OF CHLORINATION EXPERIMENTS
(PRELIMINARY PROCESS DEVELOPMENT STUDIES)

	Analysis of Product Condensed					BCl$_3$ Pro-duc-tion	Vent Gas Analysis				Recovery			Pass Yield		Overall Yield	Recycle
Expt. No.	B per cent	Cl$^-$ per cent (a)	Chlor-ine gas per cent	Total per cent	BCl$_3$ Made g. (b)	Rate lb./hr./ft.^{3}	CO per cent	CO$_2$ per cent	O$_2$ per cent	B per cent	C per cent	Cl$_2$ per cent	Overall per cent	B (c) per cent	Cl$^-$ (d) per cent	B (e) per cent	B (f) per cent
450D-41	-	-	-	-	539.0	5.96	-	25	-	-	-	-	-	-	-	-	-
43	-	-	-	-	717.4	9.74	-	-	-	-	-	-	-	-	-	-	-
45	9.17	87.64	1.45	98.26	1002	12.9	-	-	-	-	-	-	-	-	-	-	-
46	8.92	83.52	4.17	96.61	1047	14.2	-	-	-	-	-	-	-	-	-	-	-
47	8.46	80.76	9.48	98.70	709.7	5.8	-	-	-	-	-	-	-	-	-	-	-
48	8.42	79.48	9.88	97.78	1174.3	20.2	-	20	-	79.2	-	73.2	73.1	39.7	73.2		38.1
BL-1	9.17	87.90	3.09	100.16	914	22.4	0	22.7	0	84.3	67.1	53.4	64.5	35.0	60.5		47.2
2	7.1[illegible]	69.38	21.69	98.20	771.6	34.4	0	17.0	0	57.0	52.0	75.0	74.2	50.1	74.4		12.9
3	9.25	89.35	1.79	100.39	956.9	12.4	0	19.5	0	34.8	49.8	75.0	50.1	25.9	63.2		7.1
4	9.13	89.71	1.07	99.91	473.3	23.9	1.5	20.9	0	81.0	87.8	80.2	76.4	17.1	63.5		56.0
5	9.22	88.11	1.16	98.49	696.5	23.0	0	20	0	50.4	44.8	124.0	59.5	20.7	98.7		26.7
6	9.42	88.28	.54	98.24	643.4	4.84	0	30	2	55.4	51.2	84.8	58.1	35.4	73.5		18.3
7	9.10	87.95	1.62	98.67	109.2	15.77	0	0	0	55.9	95.4	74.8	64.8	24.2	64.6		28.5
8	8.59	82.95	6.81	98.35	469.1	12.1	78.5	10.75	0.75	72.8	78.7	79.9	72.0	30.4	78.6		38.8
9	9.40	85.28	0.51	95.19	792	22.8	77.7	15.8	1.0	71.5	114.5	101	88.0	33.6	76.4	50.8	33.9
10	9.35	86.96	0.29	96.60	600	26.7	-	-	-	64.6	84.5	87.3	76.7	25.8	65.6	40.3	36.1
11	8.99	87.34	0.09	96.42	159.2	6.64	86.0	1.0	0	40.1	98.2	76.5	71.8	14.6	45.2	19.5	25.1
12	9.24	86.43	2.54	98.21	710.4	42.3	-	-	-	88.5	90.0	100.0	91.5	40.3	90.3	74.7	46.1
13	8.99	85.06	4.96	99.01	917	36.8	73.5	16.7	0.2	82.3	101.5	123	95.8	23.8	92.9	54.6	56.2
14	8.55	82.75	7.43	98.73	101.9	98.0	-	-	-	116.0	99.0	98.0	97.1	28.5	70.3	116.0	78.7
15	7.04	67.99	22.96	97.99	213.4	120	70.3	22.7	1.0	109.4	92.8	90.3	95.0	39.0	56.6	105.0	63.0
16	9.01	87.23	1.11	97.35	338.1	9.8	54.0	33.0	0	72.6	103.0	95.7	89.1	17.8	63.8	37.5	52.5
17	8.29	79.09	8.19	95.57	500.5	22.3	50.0	42.6	2.0	80.4	98.1	90.3	88.8	15.3	59.3	41.8	63.2
18	.65	4.81	94.44	99.90	34.2	-		-	-	-	-	-	-	-	-	-	-
19	8.57	82.24	6.57	97.38	542.4	84	75.6	18.4	0	75.9	97.4	76.0	79.7	33.7	58.7	54.0	37.4
20	6.57	63.39	25.88	95.84	149.3	37.6	-	-	-	84.0	88.0	69.7	73.3	16.5	53.2	40.8	59.7
21	8.82	84.09	4.15	97.06	508.3	52.6	48.5	24.0	2.5	77.7	100.0	76.2	80.5	24.3	52.8	48.2	49.7
22	7.83	74.46	13.43	95.72	881	40.8	61.2	26.4	0.4	97.0	89.5	77.5	83.1	32.5	51.6	82.3	60.4
23	8.94	85.55	2.9	97.39	272	53.2	42.6	48.1	0	88.3	87.0	76.4	81.1	23.9	54.3	62.6	62
24	5.47	54.18	38.05	97.70	88.4	6.9				76.7	52.4	69.0	77.4	5.37	28.4	18.4	70.8
25	10.58	79.90	1.11	91.59	492.8	56.4	72	18	0	98.8	86.5	73.4	75.7	42.3	69.2	100	57.8
26	8.97	84.74	3.65	97.36	946.4	87	56	24	0	80.2	97.3	76.5	80.0	19.2	56.8	47	59.1
27	9.36	89.19	0.15	98.70	272	57.1	80.4	11.2	0	102	-	200	-	33.8	54.7	82.1	59
28	4.78	47.75	45.94	98.47	196.8	-	36	23	5	62	94.5	64	70.8	14	49.6	36.8	45.3
29	7.66	73.62	16.70	97.98	153.4	69.4	38	36	2	88	100	71.7	85.8	16.2	46.1	53	69.5
30	-	-	-	-	303.8	42.2	26	34	8	-	-	-	-	-	-	-	-
31	8.02	77.52	13.53	99.07	393.5	58	60	28.4	0	94	105	45	80.8	26.1	37.8	78	67.3
32	7.66	74.69	13.46	95.81	289	47.4		Orsat		86.5	89	52	>60	26.9	32.6	59.6	55
33	5.93	57.92	34.72	98.57	336.7	118		Inoperative		81	96	83	83	38	45.6	78	53

(a) Includes Cl$^-$ from BCl$_3$ and COCl$_2$
(b) BCl$_3$ recovered in condensers and water scrubber
(c) B pass yield = B product/B charged
(d) Cl pass yield = Cl product/Cl charged
(e) Overall B yield = B product/B charged minus unreacted B
(f) Recycle B = unreacted B/B charged

TABLE VI

COMPOSITION OF SOLIDS IN EFFLUENT GAS LINES

Expt. No.	Chlorine Rate cu.ft. per hr. S.T.P.	Reactor Temperature °C	Excess Carbon per cent	Analysis of Solids from Effluent Gas Lines: B per cent	Analysis of Solids from Effluent Gas Lines: Cl^- per cent	B and O in $B_3O_3Cl_3$ (a): B per cent	B and O in $B_3O_3Cl_3$ (a): O per cent	B and O in B_2O_3 (b): B per cent	B and O in B_2O_3 (b): O per cent	Total $B_3O_3Cl_3$ and B_2O_3	B as BCl_3 (c) per cent	B and O as B_2O_3 (d): B per cent	B and O as B_2O_3 (d): O per cent	Total	$\frac{B_2O_3}{B_3O_3Cl_3}$	$\frac{B_2O_3}{BCl_3}$
450D-48	7.0	730	100	24.1	15.6	4.8	7.05	19.3	42.9	89.6	1.58	22.5	50.0	89.7	2.27	4.21
BL-1	9.0	706	100	-	-	-	-	-	-	-	-	-	-	-	-	-
BL-2	11.0	736	100	22.6	8.6	2.6	3.8	20.0	44.4	79.4	0.87	21.5	48.0	79.0	4.29	7.32
BL-3	4.7	710	20	-	-	-	-	-	-	-	-	-	-	-	-	-
BL-4	9.0	723	20	24.2	15.5	4.8	7.0	19.4	43.0	89.7	1.57	22.6	50	89.7	2.28	4.25
BL-5	11.0	731	20	22.2	7.8	2.4	3.5	19.8	44.0	77.5	0.79	21.4	47.8	77.8	4.65	8.05
BL-6	1.5	717	20	23.2	20.32	6.3	9.2	16.9	37.5	90.2	2.06	21.1	47.0	90.5	1.52	3.04
BL-7	9.0	710	20	22.5	10.6	3.2	4.8	19.3	42.9	80.8	1.08	21.4	47.8	80.9	3.35	5.9
BL-8	5.0	740	200	24.7	8.0	2.5	3.6	22.2	49.2	85.5	0.8	23.9	53.0	85.7	5.06	8.7
BL-9	9.0	718	200	24.7	18.9	5.8	8.5	18.9	42.0	94.1	1.9	22.8	50.7	94.3	1.83	3.5
BL-10	12.5	719	200	25.7	5.9	1.8	2.7	23.9	53.2	87.5	0.6	25.7	57.2	89.4	7.4	12.7
BL-11	3.6	868	200													
BL-12	11.0	709	200	24.17	4.59	1.4	2.07	22.77	50.5	81.35	.47	23.7	52.6	81.36	9.1	15.1
BL-13	9.1	718	100	23.19	7.39	2.25	3.3[illegible]	20.94	46.5	80.41	.75	22.44	49.9	80.48	5.2	8.9
BL-14	8.8	693	200	18.85	5.06	1.54	2.27	17.31	38.5	64.68	.52	18.33	40.8	64.71	6.3	9.8
BL-15	8.8	730	200	18.95	3.51	1.07	1.58	17.88	39.7	63.76	.35	18.6	41.8	64.25	9.3	15.7
BL-16	3.6	624	100													
BL-17	7.6	607	100	10.12	7.50	2.29	3.37	7.83	17.4	38.39	.76	9.36	20.8	38.42	1.92	3.65
BL-18	3.2	585	100	20.72	3.78	1.15	1.7	19.57	43.5	69.7	.36	20.34	45.2	69.7	9.5	15.8
BL-19	34.0	705	100	20.43	6.02	1.84	2.17	18.59	41.3	70.46	.61	19.82	44.1	70.55	5.67	9.6
BL-20	11.5	583	100	18.29	6.43	1.96	2.9	16.33	36.3	63.92	.65	17.64	39.2	63.92	5.12	8.02
BL-21	11.5	715	100	22.39	12.02	3.67	5.41	18.72	41.6	81.42	1.22	21.17	47.0	81.41	.86	5.15
BL-22	17.8	635	200	23.66	10.48	3.2	4.72	20.46	45.5	84.36	1.06	22.60	50.2	84.34	3.58	6.3
BL-23	11.5	610	200	21.27	4.26	1.3	1.92	19.97	44.4	71.85	.43	20.84	46.4	71.93	8.6	14.4
BL-24	3.6	673	100	20.58	9.80	2.99	4.41	17.59	39.0	73.79	.99	19.59	43.5	73.88	3.29	5.9
BL-25	11.5	726	200	24.99	6.40	1.95	2.88	23.04	51.1	85.37	.65	24.34	54.1	84.49	6.6	11.1

(a) Assuming all Cl^- as $B_3O_3Cl_3$
(b) Assuming remaining boron is in B_2O_3
(c) Assuming all Cl^- as BCl_3
(d) Assuming remaining boron is in B_2O_3

TABLE VII
RELATIVE AMOUNTS OF BORON TRICHLORIDE AND WHITE SOLIDS PRODUCED

Expt. No. BL-	Cl_2 Rate cu.ft./hr. at S.T.P.	Temperature °F	BCl_3 Produced g.	B in BCl_3 g.	White Solids g.	B in White Solids per cent	B in White Solids g.	B in BCl_3/B in White Solids	Excess Carbon per cent
3	4.7	1310	957	88.2	25.9	-	-	-	20
4	9.0	1332	473	43.7	7.0	24.2	1.69	25.8	20
5	11.0	1350	697	64.3	35.0	22.2	7.76	8.3	20
6	1.5	1322	603	55.6	13.5	23.2	3.13	17.8	20
7	9.0	1310	109	10.1	10.0	22.5	2.25	4.5	20
8	5.0	1364	469	43.3	10.0	24.7	2.47	17.6	200
9	9.0	1323	793	73.2	30.0	24.7	7.4	9.9	200
10	9.5	1324	600	55.4	8.0	25.7	2.05	27.0	200
11	3.6	1593	159	14.7	8.0	25.0 (a)	2.0	7.35	200
12	11.0	1307	710	65.5	38.0	24.2	9.2	7.12	200
13	9.1	1323	917	84.6	26.0	23.2	6.03	14.0	100
16	3.6	1154	338	31.2	10.0	-	-	-	100
17	7.6	1124	501	46.2	20.0	10.12	2.02	22.8	100
18	3.2	1084	34	3.14	10.0	20.7	2.07	1.52	100
19	34.0	1302	542	50.0	22.0	20.4	4.48	11.2	100
22	17.8	1174	881	81.3	21.0	23.7	4.97	16.4	200
24	3.6	1242	88.4	8.15	3.0	20.58	.62	13.2	100
26	34	1180	946	87.3	13.0	25.05	3.25	26.8	100
28	3.65-5	1292	197	18.2	10.0	15.8	1.58	11.5	100
								Average 14.2	
				Partial Bed Experiments					
20	11.5	1082	149.3	13.8	10.0	18.29	1.83	7.5	100
21	11.5	1319	508.3	47.0	25.0	22.39	5.6	8.4	100
27	11.5	1591	272	25.1	10.0	24.17	2.4	10.5	100
29	9	1292	153.4	14.2	5.00	18.23	0.91	15.6	100
30	9	1112	303.[illegible]	28.0	41.0	20.0 (a)	8.2	3.4	100
31	9	1472	393.5	36.4	33.0	17.88	5.9	6.17	100
32	9	1112	280	26.7	12.0	22.02	2.64	10.1	100
33	12.5	1472	336.7	31.2	17.0	4.11	0.70	44.5	100

(a) Assumed

TABLE VIII

COMPOSITION OF SOLIDS IN EFFLUENT GAS LINES CORRECTED FOR METALLIC CHLORIDES

Expt. No. (a)	Temperature °F	Cl_2 Rate cu.ft./hr. S.T.P.	Excess Carbon per cent	Cl^- per cent	Ni per cent	B per cent	Fe per cent	Cl^- as $NiCl_2$ per cent	Cl^- as $FeCl_2$ per cent	$NiCl_2$ per cent	$FeCl_2$ per cent	Residual Cl^-
BL-28	1292	3.6-5.0	100.	9.96	6.96	15.77	3.22	8.42	4.1	15.4	7.3	None (b)
BL-29	1292	9.0	100.	4.72	7.24	18.23	8.18	8.76	10.4	16.0	18.6	None (b)
BL-30	1112	9.0	100	16.30	0.62	16.73	0.10	0.75	0.1	1.4	0.2	15.45
BL-31	1472	9.0	100	3.26	10.35	17.88	4.54	12.52	5.8	22.8	10.3	None (b)
BL-32	1112	9.0	100	6.42	0.80	22.02	0.10	0.97	0.10	1.8	0.2	5.35
BL-33	1472	12.5	100	0.67	37.55	4.11	0.00	45.42	0.00	83.0	0.0	0.00

(a) Carbon was added to 100 per cent excess in each experiment.

(b) Cl^- in $NiCl_2$ plus $FeCl_2$ is greater than total Cl^-.

TABLE IX
HYDROGEN CHLORIDE-BORON TRICHLORIDE WEIGHT RATIOS PROCESS DEVELOPMENT EXPERIMENTS

Expt. No.	BCl_3 Made g.	HCl Made g.	HCl / BCl_3 Wt. Ratio	H in R-1 Feed per cent
BL-13	917	224	.244	-
BL-16	338.1	153	.453	-
BL-17	500.5	186	.372	-
BL-18	34.2	21.5	.629	-
BL-19	542.4	126	.232	-
BL-24	88.4	46.4	.525	-
BL-26	946.4	294	.311	1.3
BL-28	196.8	49	.249	1.3

TABLE X
CARBON MONOXIDE-CARBON DIOXIDE RATIOS PROCESS DEVELOPMENT EXPERIMENTS

Expt. No.	Bed Height in.	Chlorine Rate cu.ft./hr. at S.T.P.	Temperature °F	CO / CO_2
BL-15	3	8.9	1346	3.1
BL-29	3	9.0	1292	1.05
BL-30	3	9.0	1112	0.77
BL-31	3	9.0	1472	2.1
BL-21	6	11.5	1319	2.02
BL-23	6	11.5	1130	0.89
BL-25	6	11.5	1341	4.0
BL-27	6	11.5	1591	7.17
BL-13	12	9.1	1323	4.4
BL-4	12	6.8	1335	0.1
BL-17	12	6.8	1124	1.18
BL-28	12	4.3	1292	1.5
BL-8	12	3.6	1360	7.3
BL-11	12	3.6	1593	86.
BL-16	12	3.6	1154	1.6
BL-19	12	34.	1302	4.1
BL-22	12	34.	1174	2.32
BL-26	12	34.	1180	2.33

TABLE XI
OPERATING CONDITIONS FOR AUXILIARY CARBON BED CHLORINATION (a)

Expt. No.	Cl_2 Rate to R-1 cu.ft./hr. at S.T.P.	Cl_2 Rate to R-2 cu.ft./hr. at S.T.P.	Solid Feed Formulation (R-1)	Form	Bed Height R-1 in.	Bed Height R-2 in.	Bed Temperature R-1 °F	Bed Temperature R-2 °F	Duration of Expt. hr.	Time Before Plug hr.	Time Excess Cl_2 Observed hr. (b)	Remarks
BL-												
34	20.0	4.0	0.100W25K150	pellets	12	-	1112	1148	0.25	0.083	0.17	
35	15.0	3.0	0.100W25K150	pellets	12	-	1292	1022	0.35	0.317		plug
36	10.0	2.0	0.100W25K150	pellets	12	-	1292	1292-1472	0.50	0.50		plug at vent line and before c-bed
37	5.0	1.0	0.100W25K150	pellets	12	-	1292	1292	1.47			plug in line tee in c-bed
38	8.0	1.6	0.100W25K150	pellets	12	-	1292	1247	0.40	0.40		
39	8.0	1.6	0.100W25K150	pellets	12	-	1292	1292	0.67	0.20		several plugs
40	8.0	1.6	0.100W25K150	pellets	12	-	1292	1292	0.833	0.67		plug between condenser
41	15.0	3.0	0.100W25K150	pellets	12	-	1292	1292	0.667	0.667		plug in c-bed
Sp. Expt.												
A-1	20.0	-	0.100W25K150	pellets	3	-	1292	-	0.25	0.25		
A-2	20.0	-	0.100W25K150	pellets	3	-	1292	-	0.184	0.0167		negligible effluent gas line solids
A-6	20.0	-	0.100W25K150	pellets	-	-	1292	-	0.333	none		negligible effluent gas line solids
BL-												
45	8.1	0.90	0.1000W25K150	pellets	6	-	1310	1310	0.70	no plug	0.25	excess Cl_2 at shutdown
46	8.1	0.90	A.100W20SuWa(80Wa)	pellets	10	-	1328	1328	0.67	0.67		plug
47	3.24	0.36	A.100W205SuWa(80Wa)	pellets	10	-	1328	1292	2.33	0.42		plug
48	5.40	0.60	A.100W205SuWa(80Wa)	pellets	10	-	1300	1454	1.42	0.50		plug at reactor
50	5.4	0.60	A.100W205SuWa(80Wa)	pellets	10	-	1200-1524	1445	1.08	0.58		
51	6.0	0.0	A100WSuWa	pellets	11	-	1418	1472	0.67	0.67		plug in trap
52	5.4	0.6	A100WSuWa	pellets	1	-	1382	1508	1.62	1.62	1.62	
53	19.20	4.80	A100WSuWa	pellets	11	-	1382	1436	0.33	no plug		
55	4.8	1.20	A100W255Wa	briquet	11	-	1292	1342	0.75	0.75	0.75	plug
56	4.8	1.20	A100W255Wa	briquet	11	-	1292	1486	1.53	0.50	1.03	plug
57(c)	6	trace	A83W20SuWa(60Wa)	briquet	11	0	1310	1517	0.83	no plug	0.83	
58	9	1.8	A83W20SuWa(60Wa)	briquet	11	24	1076	1508	1.00	0.20	0.80	
59	9	1.8	A83W20SuWa(60Wa)	briquet	11	12	1184	1544	1.00	no plug	1.0	
59R	9	1.8	A83W20SuWa(60Wa)	briquet	11	12	1184	1511	0.92	no plug	0.92	
60	15	3.0	A83W20SuWa(60Wa)	briquet	11	24	1274	1423	0.42	0.47		plug in reactor
61	15	1.5	A83W20SuWa(60Wa)	briquet	11	12	1247	1454	0.68	0.68	(b)	plug in c-bed
62	3	0.6	A83W20SuWa(60Wa)	briquet	11	12	1175	1580	1.28	no plug	1.2	
63	3	0.6	A83W20SuWa(60Wa)	briquet	11	24	1157	1542	2.08	no plug	2.0	
64	9	1.0	A83W20SuWa(60Wa)	briquet	11	12	1184	1542	0.97	no plug	0.97	
65	9	1.0	A83W20SuWa(60Wa)	briquet	11	24	1184	1511	0.75	no plug		
66	15	1.8	A83W20SuWa(60Wa)	briquet	11	24	1202	1472	0.67	0.67		plug in reactor bed
67	3	trace	A83W20SuWa(60Wa)	briquet	11	0	1256	1508	1.58	1.58	1.58	
68	15	3.0	- 3/8-1/2"	granules	11	24	1159	1472	0.67	0.67		plug in c-bed
69	3	0.6	A83W.20SuWa(60Wa)	briquet	11	6	1202	1472	1.42	no plug	0.83	
70	9	1.8	A83W.20SuWa(60Wa)	briquet	11	6	1184	1454	0.85	0.0	0.85	plug in c-bed
71	15	3.0	A83W.20SuWa(60Wa)	briquet	11	6	1202	1508	0.37	0.37	0.43	number 2 condenser plugged
72	9	trace	A83W.20SuWa(60Wa)	briquet	11	0	1220	1472	0.78	0.75	0.75	plug in crossover between R1 and R2
73	15	trace	A83W.20SuWa(60Wa)	briquet	11	0	1220	1490	0.63	no plug	0.63	
74	15	3.0	- 1/4-3/4"	granules	11	24	1292	1472	0.75	no plug	0.75	
71R	15	3.0	A83W.20SuWa(60Wa)	briquet	11	6	1382	1346	0.43	no plug	0.37	plug in c-bed
72R	9	1.8	A83W.20SuWa(60Wa)	briquet	11	0	1319	1472	0.90	0.20	0.90	plug in c-bed
76	9	1.8	A83W.20SuWa(60Wa)	briquet	11	6	1472	1508	0.33	no plug	0.33	plug in R-2 (c-bed)
79	9	1.8	A83W.20SuWa(60Wa)	briquet	11	6	1175	1454	0.42	0.42	0.42	
80	12	2.4	A83W.20SuWa(60Wa)	briquet	11	9	1175	1300	0.20	no plug	0.20	
79R	9	1.8	A83W.20SuWa(60Wa)	briquet	11	9	1220	1310	0.384	0.03	0.38	
80R	12	2.4	A83W.20SuWa(60Wa)	briquet	11	9	1166	1454	0.416	no plug	0.43	
81	15	3.0	A83W.20SuWa(60Wa)	briquet	11	9	1175	1230	0.40	no plug	0.40	
81R	15	3.0	A83W20SuWa(60Wa)	briquet	11	9	1184	1652	0.25	no plug	0.25	
82	18	3.6	A83W20SuWa(60Wa)	briquet	11	9	1094	1292	0.25	no plug		
82R	18	3.6	A83W20SuWa(60Wa)	briquet	11	9	1211	1472	0.162	no plug	0.17	
83	9	1.8	A83W20SuWa(60Wa)	briquet	11	9	1220	1436	0.450	0.03	0.45	plug in c-bed
84	9.0	1.8	A100W20SuWa	briquet	11	24	1342	1562	0.88	no plug	0.89	
85	9.0	1.8	A100W20SuWa	briquet	11	24	1232	1580	0.62	no plug	-	shutdown because of leaks
85R	14.2	1.8	A100[illegible]20SuWa	briquet	11	24	1400	1472	0.60	0.60	-	shutdown because of plug in c-bed
86	14.2	1.8	A50W20SuWa	briquet	11	24	1346	1526	0.62	no plug	0.62	
87	14.2	1.8	A50W20SuWa	briquet	11	24	1220	1526	0.23	no plug	-	shutdown because of leaks in c-bed (R-2)
87R	14.2	1.8	A50W20SuWa	briquet	11	24	1220	1436	0.50	no plug	0.50	
88	14.2	1.8	A200W20SuWa	briquet	11	24	1184	1436	0.50	no plug	0.50	
89	14.2	1.8	A20[illegible]0SuWa	briquet	11	24	1220	1490	0.67	no plug	0.67	
90	14.2	1.8	A300W20SuWa	briquet	11	24	1238	1436	0.48	no plug	0.48	
91(c)	14.2	1.8	A300W20SuWa	briquet	11	24	1202	1472	-	-	0.50	hole burned through thermowell.

Miscellaneous Experiments

Expt. No.	Cl_2 Rate to R-1	Cl_2 Rate to R-2	Solid Feed Formulation (R-1)	Form	Bed Height R-1	Bed Height R-2	Bed Temperature R-1	Bed Temperature R-2	Duration	Time Before Plug	Time Excess Cl_2	Remarks
BL-												
75	15.0	3.0	A83W20SuWa(60Wa)	briquet	11	24	1220	1512	0.58	no plug	-	grate in R-1 to support bed.
77	3.0	0.6	A100W20SuWa(60Wa)	see remarks	11	24	1346	1562	1.17	no plug	1.17	6-30 mesh powder from ground-up briquettes
78	9.0	1.8	A100W20SuWa(60Wa)	see remarks	11	24	1166	1382	0.72	0.72	0.72	-30 mesh powder from ground-up granules

(a) BL-34-56 were preliminary process development experiments.
BL-57-83 were sizing experiments
BL-84-91 were made to determine effect of amount of excess carbon.
BL-75, 77, and 78 are miscellaneous experiments.
Carbon pellets in carbon bed were used for experiments BL-34 to 91.
BL-34 to 41: 1 in. i.d. x 12 in. horizontal c-bed. Resistance wire wrapped R-1.
BL-Sp. Expt. A-6: 3 in. layer of C-pellets on top of 3 in. layer of boric oxide.carbon pellets.
BL-46 to 56: 2 1/2 in. x 25 in. horizontal c-bed.
All experiments, 3 in. i.d. x 12 in. nickel pipe R-1 was used.

(b) Elapsed time before chlorine appeared in R-2 effluent gas stream as indicated by color change of potassium iodide solution.

(c) BL-57 to 91, except BL-75: Boric oxide-carbon charge in R-1 "hot zone" only. Supported by bed of carbon pellets in cold zone. 2 1/2 in. i.d. x 25 in. vertical carbon bed.

TABLE XII
RESULTS OF CHLORINATION WITH USE OF AUXILIARY CARBON BED

Expt. No.	Analysis of Product Condensed: B per cent	Cl (a) per cent	Cl_2 per cent	$COCl_2$ per cent	Total per cent	BCl_3 Made g. (b)	BCl_3 Production Rate lb./hr./ft.^{3}	Vent Gas Analysis: CO per cent	CO_2 per cent	O_2 per cent	Recovery Pass Yield: B per cent	Cl_2 per cent	B (c) per cent	Cl (d) per cent	Overall Yield (e) B per cent
BL-															
34	-	-	-	-	-	41.47	7.15				84.4	18	2.7	6.4	14.5
35	6.34	61.03	31.82	-	99.19	375.5	46.0		Orsat		86.6	81	21.7	54	60.5
36	8.09	71.48	15.63	-	95.20	334.3	28.8				63.5	82.2	12.1	51.2	24.4
37	8.66	84.06	6.17	-	98.89	411.4	12.06				90.4	58	14.1	[illegible]9.5	57.5
38	7.99	78.37	12.3	-	98.66	235.2	25.35		Inoperative		67	91.7	15.7	62	31
39	9.0	87.53	0.94	-	97.47	363.4	23.5				85	67	28.5	54.2	58.8
40	9.12	87.98	0.6	-	97.70	433.4	22.5				77	67.9	29.3	53.6	72.1
41	8.72	83.92	5.7	-	98.34	659.9	42.5	5.4	9.4		83.4	69.5	54.7	54.5	76.7
SP Expt.															
A-1	8.89	-	-	-	-	245.0	169		Orsat		83.4	73.5	48.2	47	68
A-2	7.13	-	-	-	-	145.3	136		Inoperative		85.8	53.5	30.7	39.6	67
A-3	8.07	-	-	-	-	284.0	122				69.3	77.5	45	56	57.3
45	7.29	76.81	13.27	-	97.37	118.0	14.4	61	10.0	3.3	82	41	50	37.5	73.5
46	8.03	83.71	4.62	-	96.36	527	40.8	62.5	12.5	0	78	105	37	100	63
47	9.06	87.35	3.14	-	99.55	436	9.6	74.6	14.6	0.8	56	90	38	87	46
48	8.62	90.22	0.21	-	99.05	597	21.7	71.6	18.0	0.4	53	80	42	80	47
49	8.44	88.13	1.15	-	97.72	-	-	-	-	-	-	-	-	-	-
50	8.84	77.40	8.54	-	94.78	302	14.4	60.4	21.6	0.8	76	58	21	53	46
51	9.30	89.54	0.16	-	99.00	346	24.3	61.9	15.3	1.1	77	103	23	103	50
52	9.20	89.31	0.59	-	99.10	710	20.6	65	8.7	2.4	104	84	67	84	106
53	8.14	77.44	10.95	-	96.53	391	55.2	-	-	-	65	57	44	56	51
55	6.50	65.19	26.18	-	97.87	113	7.0	-	-	-	60	43	10	35	21
56	8.65	84.32	5.41	-	98.58	641	19.6	60.4	10.0	1.6	103	91	84	65	104
57	8.32	81.31	10.01	-	99.64	317.8	17.9	48.4	22.6	1.3	87	79	39	58	85
58	8.33	83.82	7.87	-	100.02	578.3	27.1	64	19.4	0.5	111	70	78	64	87
59	9.56	91.44	0.10	-	101.10	524.2	24.5	63.1	16.5	.97	96	56	56	56	75
59R	9.13	89.54	0.15	0	98.82	724.5	37.0	68.1	16.2	0.4	75	81	62	81	70
60	9.17	88.31	0.03	0	97.51	598	66.9	73.5	14.0	0.6	95	91	55	90	91
61	9.02	88.64	1.76	0	100.42	899.5	61.9	[illegible]	17.6	0.7	94	94	85	92	89
62	9.10	90.92	0.18	-	100.2	275	10.0	-	-	-	83	79	26	79	59
63	8.96	89.10	0.54	-	98.60	567.5	12.8	40.6	7.4	1.6	88	96	58	96	82
64	9.28	89.46	0.35	0	99.09	600.8	29.0	34.6	6.4	1.8	69	66	61	65	66
65	9.29	90.83	0.09	-	100.21	669	41.6	-	-	-	88	101	57	101	76
66	9.35	90.69	0.07	0	100.05	805.3	56.2	31.2	2.7	1.6	83	79	73	79	79
67	6.65	67.08	26.80	0.9	100.78	377.1	11.1	-	-	-	84	121	46	89.3	69
68	9.28	89.51	0.4	0	98.83	481.2	33.7	-	-	-	66	46	48	46	57
69	7.03	69.52	19.60	-	96.15	329	10.8	56.2	16.8	1.4	47	97	33	96	38
70	8.70	85.35	5.92	0.5	100.11	592.2	32.6	70.0	17.3	0.1	93	78	62	77	86
71	9.14	90.30	1.03	-	100.47	324.5	41.0	20.6	13.6	1.4	78	59	32	59	58
72	8.50	84.46	6.37	-	99.33	309.4	19.3	52	23	0	83	61	35	53	59
73	8.80	86.49	6.13	-	101.42	648.2	48.2	24.4	8.8	1.4	88	82	56	75	75
74	7.65	77.99	12.03	-	97.67	676.6	42.3	5.9	32	0	79	70	65	68	74
71R	8.64	81.61	8.20	1.8	98.95	630.3	68.1	25.4	7.8	1.2	113	102	62.5	94.1	118.2
72R	9.27	87.75	0.71	-	97.73	462.2	24.0	59	19	0	98.5	73.9	43.5	53.0	79.5
76	Sample Lost					-	-	24.6	6.8	1.2	-	-	-	-	-
79	6.86	66.31	25.08	0.3	98.31	200.5	22.5	32.8	33.6	0	108.2	73.4	23.0	57.1	150
80	4.43	45.22	50.14	0.38	99.9	136.9	32.0	0	.08	12.4	93.9	135.0	15.5	84.2	66.5
79R	7.73	75.54	13.32	-	96.59	215.7	26.4	5.4	0.0	3.8	94.4	78.7	20.2	69.6	86.9
80R	8.46	82.02	8.72	-	99.20	409.2	45.9	37	20	5	97.0	90.9	55.9	83.9	91.5
81	4.90	34.69	58.84	-	98.48	116.8	13.6	0	3.2	14.0	90.6	44.2	17.2	24.8	57.5
81R	7.89	76.60	14.40	-	98.89	216.8	40.5	0	0.6	5.2	95.0	77.4	28.6	71.6	80.0
82	2.40	25.09	69.54	-	97.03	-	-	6.0	5.2	4.8	-	-	-	-	-
82R	7.30	71.58	20.78	-	99.66	267.6	75.0	29	13	2	98.5	117.0	39.0	96.6	93.4
83	5.87	57.58	34.87	-	98.32	188.4	19.1	23	24	0.4	107.0	83.5	27.0	61.6	97.1
Experiments To Determine Effect of Amount of Excess Carbon															
84	9.32	89.22	0.52	-	99.06	635	33.6	23.1	4.9	0.9	101.9	83.5	68.8	82.7	101.7
85	9.56	90.80	0.05	0	100.41	402.4	30.6	17.6	1.9	1.0	102.1	80.4	51.3	79.6	97.1
85R	9.50	88.90	0.05	-	98.45	579.1	45.0	9.0	8.6	2.4	101.0	70.0	67.2	69.4	86.5
86	8.52	83.70	6.87	-	99.09	576.5	47.8	45.8	14.0	2.2	101.0	81.0	90.0	75.2	98.1
87	Not Sampled		-	-	-	-	-	-	-	-	-	-	-	-	-
87R	9.39	89.34	0.50	-	99.23	515.6	48.2	43.6	20.8	1.2	93.6	87.5	72.4	84.1	90.0
88	9.29	91.65	0.07	0	100.91	479.3	44.0	10.5	7.9	1.3	105.0	79.6	89.1	79.2	102.8
89	8.65	83.70	6.18	0	98.53	521	36.6	10.5	6.2	0.8	93.4	72.5	81.4	63.0	91.9
90	9.40	90.70	0.60	0	100.97	466.6	45.0	8.9	3.6	0.7	98.5	81.6	86.2	78.0	90.0
91	9.22	88.55	0.54	-	98.31	408	38.2	10	3.9	2.1	87.6	73.9	69.5	73.4	81.5
Miscellaneous Experiments															
75	9.46	90.29	0.13	0	98.88	626.6	50.3	-	14.8	0.6	102.0	67.4	57.0	67.1	100.7
77	8.86	80.13	4.70	-	94.29	276.6	11.1	11	4.6	0.2	100.0	110.5	16.8	107.2	80.1
78	9.39	90.04	0.12	-	99.55	464.2	32.9	17	10.9	0.4	84.4	79.5	31.5	79.4	64.6

(a) Includes Cl from $COCl_2$
(b) BCl_3 recovered in condenser receivers and water scrubber
(c) B pass yield = B product/B charged
(d) Cl pass yield = Cl product/Cl charged
(e) Overall B yield = B product/B charged minus unreacted B

TABLE XIII
RELATIVE AMOUNTS OF BORON TRICHLORIDE AND WHITE SOLIDS, AUXILIARY CARBON BED EXPERIMENTS

Expt. No.	Chlorine Rate R-1 cu.ft./hr.S.T.P.	Chlorine Rate R-2 cu.ft./hr.S.T.P.	Bed Height R-1 in.	Bed Height R-2 in.	Bed Temperature R-1 °F	Bed Temperature R-2 °F	BCl_3 Produced g.	B in BCl_3 g.	Boron Not Converted: Overhead Solids "O" Wt. g.	Overhead Solids "O" B per cent	Overhead Solids "O" Wt. Boron g.	Wash "W" Wt. g.	Wash "W" B per cent	Wash "W" Wt. Boron g.	Total B in O + W g.	$\frac{B_{BCl_3}}{B_{O+W}}$
BL-																
34	20.00	4.00	12.0	-	1112	1148	47	3.82	-	-	-	600	0.22	1.32	1.32	2.89
35	15.00	3.00	12.0	-	1292	1022	375.[illegible]	34.6	-	-	-	1000	0.13	1.30	1.30	26.6
36	10.00	2.00	12.0	-	1292	1292-1472	33[illegible]	30.9	-	-	-	1000	0.28	2.80	2.80	11.0
37	5.00	1.00	12.0	-	1292	1292	411.4	38.0	-	-	-	1000	0.23	2.30	2.30	16.5
38	8.00	1.60	12.0	-	1292	1247	235.2	21.7	-	-	-	1000	0.30	3.00	3.00	7.2
39	8.00	1.60	12.0	-	1292	1292	363.4	33.6	-	-	-	1000	0.56	5.60	5.60	6.0
40	8.00	1.60	12.0	-	1292	1292	433.4	39.9	-	-	-	1000	0.29	2.90	2.90	13.8
41	15.00	3.00	12.0	-	1292	1292	659.9	60.9	-	-	-	1200	0.81	8.10	8.10	7.5
Sp. Expt.																
A-1	20.00	-	3.0	-	1292	-	245.0	22.6	-	-	-	1000	0.28	2.80	2.80	8.1
A-2	20.00	-	3.0	-	1292	-	145.3	13.4	-	-	-	1000	0.11	1.10	1.10	12.2
A-6	20.00	-	-	-	1292	-		-	-	-	-	1000	0.24	2.40	2.40	-
BL-																
45	8.10	0.90	6.0	-	1310	1310	118.0	10.9	-	-	-	-	-	-	-	-
46	8.10	0.90	10.0	-	1328	1328	527.0	48.6	-	-	-	-	-	-	-	-
47	3.24	0.36	10.0	-	1328	1292	436.0	40.3	-	-	-	-	-	-	-	-
48	5.40	0.60	10.0	-	1300	1454	597.0	55.1	-	-	-	-	-	-	-	-
50	5.40	0.60	11.0	-	1200 - 1524	1445	302.0	27.8	-	-	-	-	-	-	-	-
51	6.00	0.00	11.0	-	1418	1472	346.0	31.9	-	-	-	-	-	-	-	-
52	5.40	0.60	11.0	-	1382	1508	710.0	65.5	-	-	-	-	-	-	-	-
53	19.20	4.80	11.0	-	1382	1436	391.0	36.1	-	-	-	-	-	-	-	-
55	4.80	1.20	11.0	-	1292	1342	113.0	10.4	-	-	-	-	-	-	-	-
56	4.80	1.20	11.0	-	1292	1486	641.0	59.2	-	-	-	-	-	-	-	-
57	6.00	trace	11.0	0	1310	1517	317.8	29.3	36.7	2.26	0.83	1378	0.29	3.99	4.83	6.1
58	9.00	1.80	11.0	24	1076	1508	578.3	53.5	-	-	-	1389	0.15	2.08	2.08	25.8
59	9.00	1.80	11.0	12	1184	1544	524.2	48.4	-	-	-	700	0.16	1.12	1.12	43.1
59R	9.00	1.80	11.0	12	1184	1511	724.5	66.9	-	-	-	1405	0.05	0.70	0.70	95.5
60	15.00	3.00	11.0	24	1274	1423	598.0	55.2	-	-	-	1455	0.073	1.10	1.10	50.2
61	15.00	1.5	11.0	12	1247	1454	899.5	84.8	-	-	-	1488	0.14	2.1	2.1	40.5
62	3.00	0.6	11.0	12	1175	1580	275	25.4	-	-	-	309	0.12	0.371	0.371	68.5
63	3.00	0.6	11.0	24	1157	1542	567.5	52.4	-	-	-	271	0.25	0.7	0.7	75.0
64	9.00	1.0	11.0	12	1184	1542	600.8	55.5	-	-	-	157	0.28	0.44	0.44	126.2
65	9.00	1.0	11.0	24	1184	1511	669	61.8	-	-	-	1042	0.37	3.9	3.9	15.9
66	15.00	1.8	11.0	24	1202	1472	805.3	74.4	-	-	-	1450	0.26	2.8	2.8	26.5
67	3.00	trace	11.0	0	1256	1508	377.1	34.8	13.5	15.1	2.04	364	0.26	0.46	3.0	11.6
68	15.00	3.0	11.0	24	1159	1472	481.2	44.3	-	-	-	1446	0.17	2.5	2.5	17.8
69	3.00	0.6	11.0	6	1202	1472	329	30.4	-	-	-	145[illegible]	0.005	0.8	0.8	38.1
70	9.00	1.8	11.0	6	1184	1454	592.0	54.6	-	-	-	1525	0.089	1.36	1.36	40.2
71	15.00	3.0	11.0	6	1202	1508	324.5	30.0	-	-	-	171	0.07	0.12	0.12	25.0
72	9	trace	11.0	0	1220	1472	309.4	28.6	59	3.7	2.2	1485	0.20	2.97	5.12	5.59
73	15	trace	11.0	0	1220	1490	648.2	59.8	47.4	4.5	2.13	1430	0.38	5.44	7.57	7.92
74	15	3.0	11.0	24	1292	1472	676.6	62.5	-	-	-	1495	0.093	1.39	1.39	44.9
71R	15	3.0	11.0	6	1382	1346	630.[illegible]	58.2	-	-	-	1710	0.146	2.49	2.49	23.4
72R	9	1.8	11.0	0	1319	1472	462.2	42.6	35	0.153	0.54	1585	0.23	3.7	4.24	10.1
76	9	1.8	11.0	6	1472	1508	-	-	-	-	-	-	-	-	-	-
79	9	1.8	11.0	6	1175	1454	200.5	18.5	-	-	-	597	0.053	0.316	0.316	58.6
80	12	2.4	11.0	9	1175	1300	136.9	12.6	-	-	-	126	0.016	0.02	0.02	630
79R	9	1.8	11.0	9	1220	1310	215.7	19.9	-	-	-	1700	0.019	0.3	0.3	66.4
80R	12	2.4	11.0	9	1166	1454	409.2	37.8								
81	15	3.0	11.0	9	1175	1296	116.8	10.8	-	-	-	1475	0.065	0.96	0.96	11.3
81R	15	3.0	11.0	9	1184	1652	216.8	20.0	-	-	-	-	-	-	-	-
82	18	3.6	11.0	9	1094	1292	-	-	-	-	-	-	-	-	-	-
82R	18	3.6	11.0	9	1211	1472	267.6	24.7	[illegible]	7.28	0.1	247	0.039	0.1	0.2	123.5
83	9	1.8	11.0	9	1220	1436	188.4	17.0	-	-	-	208	0.029	0.1	0.1	17.0
Experiments to Determine Effect of Amount of Excess Carbon																
84	9.0	1.8	11.0	24	1342	1562	635	58.6	-	-	-	400	0.059	0.25	0.25	235
85	9.0	1.8	11.0	24	1232	1580	402.4	37.2	-	-	-	452	0.085	[illegible]	0.38	98
85R	14.2	1.8	11.0	24	1400	1470	579.1	53.4	-	-	-	1597	0.18	[illegible]	2.87	18.7
86	14.2	1.8	11.0	24	1346	1526	576.5	53.2	-	-	-	2000	0.08	1.6	1.6	33.3
87	14.2	1.8	11.0	24	1220	1526	-	-	-	-	-	-	-	-	-	-
87R	14.2	1.8	11.0	24	1220	1436	515.6	47.6	-	-	-	1680	0.073	1.2	1.2	39.7
88	14.2	1.8	11.0	24	1184	1436	479.3	44.2	-	-	-	1400	0.098	1.3	1.3	34
89	14.2	1.8	11.0	24	1220	1490	521	48.2	-	-	-	1670	0.26	4.34	4.34	11.1
90	14.2	1.[illegible]	11.0	24	1238	1436	466.6	43.1	-	-	-	1300	0.24	3.1	3.1	
91	14.2	1.[illegible]	11.0	24	1202	1472	408	37.7	-	-	-	1670	0.04	0.70	0.70	53.9
Miscellaneous Experiments																
75	15.0	3.0	11.0	24	1200	1512	626.6	57.8	-	-	-	219	0.08	0.18	0.18	32.1
77	3.0	0.6	11.0	24	1346	1562	276.6	25.5	-	-	-	195	0.2[illegible]	0.41	0.18	141.6
78	9.0	1.8	11.0	24	1166	1382	464.3	42.8	-	-	-	530	0.02	0.11	0.11	390

AD 200541

Armed Services Technical Information Agency

ARLINGTON HALL STATION
ARLINGTON 12 VIRGINIA

FOR
MICRO-CARD
CONTROL ONLY

2 OF 2

TABLE XIV

OPERATING CONDITIONS FOR CHLORINATION WITH USE OF SPHERICAL FEED (a)

Expt. No.	Cl_2 Rate: to Reactor R-1 cu.ft./hr. S.T.P.	Cl_2 Rate: to C-Bed cu.ft./hr. S.T.P.	Solid Feed: Formulation	Solid Feed: Form	Bed Temperature B-1 °F	Bed Temperature C-Bed °F	Duration of Expt. hr.	Time Before Plug hr.	Remarks (c)	
BL-										
108	9.0	1.8	A83W20SuWa(60Wa)	briquettes	1166	1319	0.685	0.216	Excess Cl_2 at .1 hr.	(b)
108R	9.0	1.8	A83W20SuWa(60Wa)	briquettes	1265	1337	0.750	0.133	Excess Cl_2 at 0.51 hr.	(b)
109	9.0	1.8	A83W20SuWa(60Wa)	briquettes	1183	1333	0.885	0.333	Excess Cl_2 at shutdown	(b)
109R	9.0	1.8	A83W20SuWa(60Wa)	briquettes	1274	1259	0.700	0.500	Excess Cl_2 at 0.67 hr.	(b)
110	9.0	1.8	A100W	1/4" granules	1211	1391	0.618	0.618	Plug in reactor	(b)
110X	9.0	1.8	A100W	1/4" granules	1220	1382	-	-		
112	9.0	1.8	A100W	1/8" granules	1211	1328	0.417	none	Plug	(b)
112R	9.0	1.8	A100W	1/8" granules	1183	1463	1.000	none		
113	9.0	1.8	A100W	1/8" granules	1211	1409	0.416	0.416	Plug at flange	(b)
109RR	9.0	1.8	A83W20SuWa(60Wa)	briquettes	1220	1436	0.750	0.367	Plug in condensers	
114	9.0	1.8	A83W20SuWa(60Wa)	briquettes	1374	1436	0.650	none	Petroleum Coke in C-Bed Excess Cl_2 at shutdown	
115RR	9.0	1.8	A83W20SuWa(60Wa)	briquettes	1198	1421	0.667	0.667	Plug in spool in C-Bed	
116	9.0	1.8	A83W20SuWa(60Wa)	briquettes	1274	1517	1.083	NoPlug	Excess Cl_2 at 0.92 hr.	
					1391	1571				
					1346	1481				
					1337	1417				
117	9.0	1.0	A83W20SuWa(60Wa)	briquettes	1211	1453	1.000	1.000		(b)
118	9.0	1.8	A100W	1/8 to 1/4 inch granules	1196	1538	0.833	0.367		
119	9.0	2.2	A100W	1/8 to 1/4 inch granules	1220	1537	0.600	0.483	Number 2 Condenser plugged	(b)
120	3.0	0.6	A100W	1/8 to 1/4 inch granules	1202	1445	2983	1.700	Condenser plugged	(b)
					1355	1476				
					1355	1517				
					1346	1534				
					1328	1562				

TABLE XIV (Continued)

OPERATING CONDITIONS FOR CHLORINATION WITH USE OF SPHERICAL FEED a) Continued

Expt. No.	Cl_2 Rate: to Reactor R-1 cu.ft./hr. S.T.P.	Cl_2 Rate: to C-Bed cu.ft./hr. S.T.P.	Solid Feed: Formulation	Solid Feed: Form	Bed Temperature R-1 °F	Bed Temperature C-Bed °F	Duration of Expt. hr.	Time Before Plug hr.	Remarks (c)
121	9.0	1.8	A100W	1/4 to 1/2 inch granules	1263 140 1292	1432 1470 1508	1.600	0.633	Plug at scrubber (b)
122	3.0	0.6	GS-1-A100W	1/8 to 1/4 inch granules	1193 1453	1418 1481	1.750	0.750	Plug in overhead line (b)
123	12.0	2.4	GS-1-A100W	1/8 to 1/4 inch granules	1238 1358 1272	1409 1400 1472	0.820	0.150	Plug in crossover
124	4.8	0.15	BA-112A-83W -20SuWa(60Wa)	briquettes	1222 1274 1292	1450 1470 1508	1.000	NoPlug	
125	9.0	2.5	GS-1-A100W	1/8 to 1/4 inch granules	1222 1418	1488 -	1.050	0.830	
126	9.0	2.5	BA-112A-83W -20SuWa(60Wa)	briquettes	1364	1490	0.580	0.330	Plug in overhead line and first condenser.
127	9.0	2.5	BA-112A-83W -20SuWa(60Wa)	briquettes	1245	1598	0.500	NoPlug	Thermowell turned off
128	9.0	2.5	BA-112A-83W -20SuWa(60Wa)	briquettes	1228 1342 1302	1445 1482 1508	0.90	0.11	Excess Cl_2 at shutdown
129	15.0	4.5	G-S-2-A-100W	1/8 to 1/4 inch granules	1247	1476	0.50	NoPlug	Overhead filled with solid
130	15.0	4.5	G-S-2-A-100W	1/8 to 1/4 inch granules	1224 1428 1375	1482 1478 1382	0.60	0.45	Excess Cl_2 at shutdown
131	15.0	4.5	G-S-2-A-100W	1/8 to 1/4 inch granules	1230 1442 1409	1490 1588 1604	0.87	0.33	Plug in number 3 condenser

TABLE XIV (Continued)

OPERATING CONDITIONS FOR CHLORINATION WITH USE OF SPHERICAL FEED (a) Continued

Expt. No.	Cl_2 Rate to Reactor R-1 cu.ft./hr. S.T.P.	Cl_2 Rate to C-Bed cu.ft./hr. S.T.P.	Solid Feed Formulation	Solid Feed Form	Bed Temperature R-1 °F	Bed Temperature C-Bed °F	Duration of Expt. hr.	Time Before Plug hr.	Remarks (c)
132	24.0	7.2	G-S-2-A-100W	1/8 to 1/4 inch granules	1336	1496	0.22	0.22	Plug in C-Bed
133	24.0	7.2	G-S-3-100W	1/8 to 1/4 inch granules	1346	1481	0.13	0.13	Plug in overhead line and number one condenser
134	24.0	7.2	G-S-3-100W	1/8 to 1/4 inch resintered granules	1247 1256	1535 1148	0.42	NoPlug	Excess Cl_2 at shutdown
135	24.0	7.2	G-S-4 A-100W	1/8 to 1/4 inch resintered granules	1202 1355	1499 1553	0.39	0.20	Excess Cl_2 at shutdown
136	15.0	4.5	BA-112A-83W 20SuWa(60Wa)	briquettes	1256 1364 1292	1517 1537 1553	0.53	0.15	Plug in metal line leading out of C-Bed
137	15.0	4.5	BA-112A-83W 20SuWa(60Wa)	briquettes	1283	1489	0.20	NoPlug	Overhead line cracked
137R	15.0	4.5	BA-112A-83W 20SuWa(60Wa)	briquettes	1427	1517 1499	0.45	0.20	Plug in first condenser
138	24.0	7.2	BA-112A-83W 20SuWa(60Wa)	briquettes	1260	1444	0.08	0.08	
138R	24.0	7.2	BA-112A-83W 20SuWa(60Wa)	briquettes	1141	1608	0.13	0.08	Thermowell blew out

(a) R-1 bed - 11 inches of boric oxide-carbon feed in hot zone of R-1, supported by carbon pellets in cold zone. R-2 bed - 24 inches of carbon pellets except where noted.
(b) Carbon briquettes in carbon bed
(c) Excess chlorine time. Time elapsed before chlorine appeared in effluent gas stream as indicated by change in color of potassium iodide solution.

TABLE XV

RESULTS OF CHLORINATION OF SPHERICAL FEED

Expt. No.	Analysis of Product Condensed: B per cent	Cl(a) per cent	Cl_2 per cent	$COCl_2$ per cent	Total per cent	HCl Made lb.	BCl_3 Made lb.(b)	BCl_3 Product Rate lb./hr./ft.^{2} (g)	Vol ume ft.^{3}	Vent Gas Analysis: CO per cent	CO_2 per cent	O_2 per cent	Recovery: B per cent	Cl per cent	Pass Yield: B(c) per cent	Cl(d) per cent	Overall Yield B(e) per cent
BL.																	
108	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
108R	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
109	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
109R	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
110	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
110R	Not Chlorinated						-	-	Not Chlorinated								
111	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
111R	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
113	Sample Not Analyzed				-				[illegible]	[illegible]	[illegible]	[illegible]				-	
113RR									[illegible]	[illegible]	[illegible]	[illegible]					
115	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
115RR	[illegible]	[illegible]	trace	-	[illegible]		[illegible]	[illegible]	(f)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
116	[illegible]	[illegible]	[illegible]	-	[illegible]		[illegible]	[illegible]	(f)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
117	[illegible]	[illegible]	[illegible]	-	[illegible]		[illegible]	[illegible]	(f)				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
118	Not Sampled				-		-	-	(f)	41.6	15.6	6.6		-			
119	9.54	89.07	0	0	98.61		354	1.30	(f)	50.4	23.6	6.5	63.0	62.3	33.10	60.14	40.4
120	9.59	89.66	0	0	99.25		1023	.732	(f)	70	13.6	1.0	112.1	76.3	95.9	75.3	150.7
121	9.37	87.21	0	0	96.58		567	.781	(f)	33.6	29.2	20.4	111.4	60.1	67.03	39.99	78.72
122	9.51	88.69	0	0	99.20		397	.427	(f)	58.2	16.5	6.6	90.20	67.80	37.20	72.1	65.9
123	9.64	88.47	0.24	0	99.35		772	2.05	(f)	62.2	11.8	1.3	96.06	71.69	60.93	71.4	94.2
124	9.40	88.86	trace		99.26		247	.545	(f)	19.6	7.7	19.6	69.0	65.30	24.8	58.1	36.9
125	9.46	89.65	0	-	99.11		1020	2.15	(f)	39.4	24	1.0	112.5	94.36	100.4	94.3	110.0
126	Not Sampled						-	-	(f)	44	27.6	4.0				-	
127	No Analysis				-		-	-	(f)		22.0	8.0	-			-	
128	No Analysis				-		-	-	(f)	52.4	26.0	2.0				-	
129	9.55	88.50	0	-	98.05		495	2.16	(f)	49.2	21.6	0.8	78.01	59.35	51.16	59.83	64.6
130	9.32	87.88	1.88		99.08		708	2.59	(f)	45.0	13.0	0	84.95	72.56	86.27	72.54	90.8
131	9.44	89.22	0	-			685	1.74	(f)	46.7	17.3	0	90.98	48.02	73.66	48.0	75.35
132	9.40	88.36	0	-			380	3.34	(f)	No Orsat			17.40				
133	Not Sampled				-		-	-	(f)	No Orsat			-	-		-	-
134	8.98	86.42	3.66	-			755	3.95	(f)	37.0	22.0	2.0	120.17	68.39	82.16	65.92	125.10
135	9.43	89.39	0.19	-			565	3.13	(f)	26.4	14.7	5.2	95.52	51.44	56.44	51.26	85.9
136	No Analysis (Sample Bombleaked)								4.65	-	?	9.6					
137	No Analysis (Sample Bombleaked)								0.988	21.6	25.2	1.6					
137R	9.42	88.50	0.16	trace			529	2.50	4.09	34.7	20.4	1.4	135.6	67.74	85.33	67.61	149.8
138	Not Sampled								1.31	-	-	-					
138R	Not Sampled								0.88		-	-					

(a) Includes Cl^- from phosgene
(b) Boron trichloride recovered in condenser receivers and water scrubber
(c) B pass yield = B product/B charged
(d) Cl pass yield = Cl product/Cl charged
(e) Overall yield = B product/B charged minus unreacted B
(f) No wet-test meter
(g) Experiments 114 to 126, BCl_3 production rate is given in lb./hr. (not lb./hr./ft.^{2})

TABLE [illegible]

[illegible]

Exp. No.	[illegible]	[illegible]	R-1 Feed Composition	R-2 Bed Height in.	Bed Temperatures °F		Duration of Expt. hr.	Time Before Plug hr.	Time Before Ch. Charged hr.	Remarks
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]		[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]		[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	No Plug	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	No Plug	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	No Plug		[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	No Plug		[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible] Plug in effluent gas line.
[illegible]	[illegible]	[illegible]	[illegible]	24	[illegible]	[illegible]	[illegible]	No Plug	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	No Plug	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible] from BL [illegible], R-2	[illegible]	[illegible]	[illegible]	[illegible]	No Plug	[illegible] Onstream Time	[illegible]
	[illegible]	[illegible]	[illegible] from BL [illegible], R-2	[illegible]	[illegible]	[illegible]	[illegible]	No Plug		[illegible] Plug in effluent gas line
[illegible]	[illegible]	[illegible]	A-100W (1/8-1/4")	24	[illegible]	[illegible]	0.75	No Plug	0.66	
[illegible]	[illegible]		A-100W [illegible]	[illegible]	[illegible]	[illegible]	0.75	No Plug	0.12	
[illegible]		[illegible]	A-100W [illegible]	24	[illegible]		0.66	[illegible]	0.47	
165	[illegible]	[illegible]	A-100W (1/8-1/4")	6	[illegible]		0.75	No Plug	0.38	
166	[illegible]	[illegible]	A-100W (1/8-1/4")	24	[illegible] 1193 1130		0.70	No Plug	0.30	
167	15.0	0	A-100W (1/8-1/4")	18	1382 1292		0.75	No Plug	0.37	
168	15.0	0	A-100W (1/8-1/4")	12	1418 1292 1175		0.75	No Plug	0.33	
169	15.0	0	A 100W (1/8-1/4")	6	1274		0.41	0.41	0.22	Plug in lines.
170	15.0	0	A 100W (1/8-1/4")	24	1292 1292 1220 1157	637 608 608 590	0.88	No Plug	0.25	
171	15.0	0	A 100W (1/8-1/4")	24	1337 1256	428 436	0.75	No Plug	0.82	
172	15.0	0	A 100W (1/8-1/4")	24	1355	692	0.33	0.28	-	Plug in effluent gas line.
193	9.0	0	A 100W (1/8-1/4")	24	1382	194	0.57	0.57	-	Plug in R_1 and R_2
195	9.0	0	A 100W (1/8-1/4")	24	1296	226	0.47	None	0.25	
197	9.0	0	A-100W (1/8-1/4")	24	1364	268	1.0	None	<0.50	
198	9.0	0	A-100W (1/8-1/4")	24	1337	275	0.75	None	0.65	
199	9.0	0	A-100W (1/8-1/4")	24	1286	239	0.30	0.30	-	
200	9.0	0	A-100W (1/8-1/4")	24	1258	225	1.0	None	0.33	
201	9.0	0	A-100W (1/8-1/4")	24	1276	248	1.0	None	0.17	

(a) R-1 bed height - 11 in. boric oxide-carbon feed in hot zone supported by carbon pellets in cold zone.
(b) Experiments BL-146 to 154 inclusive have the same formulation, A-100W.
(c) A.150W25,8 SuWa (68,4Wa) in R-2 for experiments BL-162 to 172.
(d) Granules 1/8-1/4 in. diameter used in all experiments except BL-156 and 157 in which briquets were used.

TABLE XVII

RESULTS OF CHLORINATION WITH USE OF COLD AUXILIARY BORIC OXIDE-CARBON BED

Expt. No.	Analysis of Product Condensed					HCl Made	BCl$_3$ Made	BCl$_3$ Production Rate	Vent Gas Volume	Vent Gas Analysis			Recovery		Pass Yield		Overall Boron Yield
	B	Cl$^-$	Cl$_2$	COCl$_2$	Total					CO	CO$_2$	O$_2$	B	Cl$_2$	B	Cl$^-$	
BL-	per cent	per cent	per cent	per cent	per cent	g.	g.	lb./hr.	ft.^{3}	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
146	9.16	90.07	0	0	99.23	Not Calculated	286	1.65	3.35	-	-	-	88.23	54.9	27.0	54.90	56.5
147	Run No Good - Not Sampled							-	1.06	-	-	-	-	-	-	-	-
148	8.93	86.73	3.30	0.1	98.99		428	2.85	3.35	-	-	-	120.6	100.0	49.3	97.7	93.7
149	8.40	80.70	9.23	0.4	98.54		728	1.95	5.68	57.6	31.7	0.5	87.47	64.8	73.0	62.4	80.2
150	Run No Good - Not Sampled							-	.74	-	-	-	-	-	-	-	-
151	8.42	81.76	7.97	0.2	98.21		467	2.66	2.89	50.9	24.9	1.4	91.6	74.8	57.2	68.92	79.0
152	9.16	89.61	0.11	0	98.88		283	1.30	3.18	28.0	27.1	0	95.10	45.19	32.5	45.02	85.0
153	9.12	88.73	0.66	0.07	98.43		597	2.02	6.85	41.8	38.8	0.2	95.50	53.74	59.4	51.39	79.3
154	7.50	76.78	14.63	0.4	99.02		578	1.95	4.87	25.7	43.2	1.8	100.25	78.18	60.5	66.93	84.5
155	6.86	65.27	25.51	0.2	97.70		688	1.83	6.99	45.8	42.2	1.2	104.02	78.15	72.7	57.84	95.1
156	5.54	53.17	38.78	0.7	97.69		509	1.49	5.35	16.5	31.7	2.5	142.3	79.85	85.0	48.25	104.5
157	8.41	81.81	8.97	0.7	99.39		814	2.24	4.98	26.9	45.6	2.4	134.27	72.47	93.5	68.81	110.0
162	8.93	86.7	2.92	0.25	98.62		321	.95	4.45	47	26.6	1.4	93.1	45.9	80.5	45.0	31.0
163	6.72	63.0	27.9	0.40	97.73		589	1.73	5.51	26.8	70.1	4.2	56.9	39.6	73.5	72.4	82.2
164	7.41	71.5	19.5	1.0	98.69		481	1.68	4.38	15.8	15.0	1.0	93.7	69.8	60.3	56.3	69.7
165	1.56	26.4	67.5	0.25	95.53	30.8	158	.47	2.68	-	-	-	61.0	76.0	19.8	25.7	22.8
166	4.83	47.6	45.9	0.25	98.40	88.9	390	1.23	4.27	25.1	18.7	1.3	89.9	82.3	48.5	47.1	58.3
167	7.51	73.9	15.2	0.30	96.69	26.2	536	1.57	4.27	29.8	38.9	2.6	94.9	60.5	66.7	50.7	70.6
168	6.95	66.2	25.5	0.43	98.77	49.7	581	1.71	4.84	27.3	24.7	1.3	100.8	71.8	72.0	55.8	88.2
169	8.86	85.8	4.06	0.17	98.77	24.0	369	1.93	3.14	17.4	32.8	2.4	71.3	65.3	45.8	62.5	49.0
170	6.33	60.4	32.9	0.50	99.77	33.2	541	1.63	4.17	12.7	32.2	2.0	103.8	77.9	62.1	51.9	72.2
171	5.97	56.8	35.2	0.70	98.10	77.1	497	1.46	4.23	34.5	20.0	8.3	111.4	79.3	88.2	51.5	105.2
172	9.51	90.2	0.05	0.10	99.79	45.8	286	1.96	-	30.8	28.0	2.0	93.0	69.2	35.0	69.1	66.4
193	9.32	90.3	0.18	trace	99.80	49.7	276	1.14	2.86	40.4	17.4	3.6	86.4	78.2	44.9	57.0	62.2
195	8.53	81.9	6.64	0.54	97.22	71.2	168	0.79	-	-	-	-	103.4	70.8	25.4	40.9	56.3
197	6.61	62.8	29.2	0.24	98.68	29.7	478	0.97	-	No Orsat Analysis			102.0	81.1	66.6	52.3	77.6
198	-	-	-	trace	-	20.2	-	-	-	No Orsat Analysis			-	-	-	-	-
199	-	-	-	0.0	-	52.7	-	-	-	No Orsat Analysis			-	-	-	-	-
200	6.18	60.[illegible]	32.4	0.43	98.70	59.9	452	.995	-	No Orsat Analysis			89.5	86.6	46.7	49.1	50.5
201	6.64	63.[illegible]	28.1	0.5	98.58	64	435	0.96	-	-	-	-	101	62.9	58.6	47.7	60.9

TABLE XVIII

RELATIVE AMOUNTS OF BORON TRICHLORIDE AND WHITE SOLIDS WITH COLD AUXILIARY BORIC OXIDE-CARBON BED (a)

Expt. No. BL	Chlorine Rate cu ft / hr, S.T.P.	Bed Temperature R-1 °F	Bed Temperature R-2 °F	BCl_3 Produced g	% B to BCl_3 Produced (b)	% B to Waste Solids (b)	B_{BCl_3} / $B_{white\ solids}$
[illegible]	15.0	1415		706	75.4	0.08	[illegible]
[illegible]	15.0	1375	219	620	99.6	0.13	[illegible]
[illegible]	15.0	1381 1400 1249	219 162 356	720	67.1	0.16	[illegible]
150	15.0	1400	269	....Not Sampled....			
151	15.0	1346 1337 1247	257 293 330	667	63.1	0.00	539
152	15.0	1301	207	283	26.1	0.10	261
153	15.0	1292 1436	212 266	597	55.1	0.10	551
154	15.0	1320 1320 1220	203 311 347	576	56.3	0.10	563
155	15.0	1435 1309 1157	266 320 360	688	63.5	0.50	127
156	15.0	1310 1337 1247	185 275 329	509	46.9	0.24	195
157	15.0	1270 1330 1235	239 347 401	814	75.0	0.0	1075
162	15.0	1320 1310	343 375	322	29.68	.42	70.7
163R	15.0	1300 1379	345 444	591	54.5	1.16	47.0
164	15.0	1350 1350	-	481	44.4	.73	60.8
165	15.0	1317	-	158	14.6	.47	31.1
166	15.0	1353 1193 1130	-	390	36.0	.10	360
167	15.0	1382 1242	-	535	49.4	.07	705
168	15.0	1418 1292 1175	-	582	53.7	.20	274
169	15.0	1274	-	369	34.0	.31	110
170(c)	15.0	1292 1292 1220 1157	637 608 608 590	542	50.0	2.86	17.5
171(c)	15.0	1337 1256	428 436	497	45.9	.31	148
172(c)	15.0	1355	692	286	26.4	1.06	24.9
193	9.0	1382	194	289	26.6	1.0	26.6
195	9.0	1296	226	197	18.2	0.1	182
197	9.0	1364	268	481	44.4	0.1	444
200	9.0	1258	225	452	41.7	0.1	417
201	9.0	1276	248	435	40.0	0.1	400

(a) Bed Height R-1, 11 inches of boric oxide-carbon feed in hot zone, supported by carbon pellets in cold zone. R-2, 24 inches in all experiments except BL-165 and 169, 6 inches; BL-167, 18 inches, and BL-168, 12 inches.

(b) Includes boron in solids condensed in effluent gas lines, and boron recovered in wash.

(c) Boric oxide-carbon bed temperatures varied in experiments BL-170 to 172.

TABLE XIX

DIRECT CHLORINATION OF CARBON BED VERSUS UNHEATED FILTER BED (FULL R-1 BED EXPERIMENTS ONLY)

Description of Process	Expt. No. BL-	Boron Pass Yield per cent	Boron Over-all Yield per cent	Boron Recovery per cent	Chlorine (a) Pass Yield per cent	Chlorine (a) Recovery per cent	Condensed Product Impurities Cl_2 per cent	Condensed Product Impurities $COCl_2$ per cent	BCl_3 (b) Production Rate lb./hr.	P_{BCl_3} / $P_{[illegible]}$
Direct Chlorination of										
1. $B_2O_3 \cdot C$ Pellets	-	29 (c)	50	73	65	84	0.5-20 (d)	Not Analyzed	1.99	14
2. $B_2O_3 \cdot C$ Briquets	-	44	72	78	62	83	0. -27	0.0 to 0.9	2.07	61
With Carbon Bed at 1470°F										
1. $B_2O_3 \cdot C$ Briquets in R-1	-	74	88	95	70	79	0.07-7.9	0	2.38	89 (e)
2. $B_2O_3 \cdot C$ Granules in R-1	-	76	91	99	65	-	0 -3.7	0	2.38	-
With unheated filter bed										
1. $B_2O_3 \cdot C$ Granules in R-1, B_2O_3 Briquets in R-2	148 to 155	58	85	99	65	71.4	0.1-26	0.0 to 0.4	2.08	990
2. Spent Briquets from R-2 in R-1: Fresh Briquets in R-2	156 and 157	89	111	138	57	-	9.0-39	0.7	1.67	103%
3. Same as 1.	193 to 201	49	61.9	96.5	49.5	-	0.10-32.4	0.0 to 0.5	1.62(f)	29%

(a) Based on total Cl_2 fed (R-1 and R-2)
(b) Based on Cl_2 to R-1 only at 15 cu.ft./hr. at S.T.P.
(c) Relatively low because BOC pellets in cold zone.
(d) Not more than 10 per cent of total experiments gave product analysis of Cl_2 outside this range.
(e) 6 to 24 in. C-Beds
(f) Run at 9.0 cu.ft./hr. at S.T.P. production rate 0.97 lb./hr.

TABLE [illegible]

[illegible] RUNS FOR CHLORINATION WITH USE OF CHLORINE PREHEATER (a)

Expt No.	Cl_2 Rate [illegible]	Feed Formulation (b)		Temperature of Preheater Reactor: Wall °F	Cl_2 Out °F	Cl_2 In °F	Bed °F	Duration of Expt, hr	Remarks	
91										
92	9	AB1W20SuWa(60Wa)	Batch, .01	1612	565	521	1112	1.92		
92R	9	AB1W20SuWa(60Wa)	Batch, .01	1612	600	620	1116	1.30		
96	9	AB1W20SuWa(60Wa)	Batch, .01	1512	651	675	1161	0.50		
99	9	AB1W20SuWa(60Wa)	Batch, .01			656	1122	0.32	Cold Preheater	(c)
15R										
18	9	AB1W20SuWa(60Wa)	Batch, .105		275		1472	0.50	Cold Preheater	(c)
19	9	AB1W20SuWa(60Wa)	Batch, .105		275		1121	0.83	Cold Preheater	(c)
20	9	AB1W20SuWa(60Wa)	Batch, .105		620		1310	0.67	Cold Preheater	(c)
21	9	AB1W20SuWa(60Wa)	Batch, .105		522		1001	0.53	Cold Preheater	(c)
22	[illegible]	AB1W20SuWa(60Wa)	Batch, .105		530		1090	0.55	Cold Preheater	(c)
23	9	AB1W20SuWa(60Wa)	Batch, .105		602		1025	0.83	Cold Preheater	(c)
[illegible]										
101	[illegible]	AB1W20SuWa(60Wa)	Batch, .105				1092	0.5	Cold Preheater	
102	9	AB1W20SuWa(60Wa)	Batch, .105		506		1200	0.75	Cold Preheater	
103	9	AB1W20SuWa(60Wa)	Batch, .105		610		1314	0.67	Cold Preheater	
104	[illegible]	AB1W20SuWa(60Wa)	Batch, .105		539		1027 (d)	3.98	Cold Preheater	
103R	9	AB1W20SuWa(60Wa)	Batch, .105		455		1252	0.67	Both flue gas blower and R-1 heat supply off	
105	9	AB1W20SuWa(60Wa)	Briquets				1292	0.17	Cold Preheater	(c)
105R	9	AB1W20SuWa(60Wa)	Briquets				1310	0.80	Cold Preheater	(c)
106R	[illegible]	AB1W20SuWa(60Wa)	Briquets	1498	986	466	1102	0.83		
106RR	9	AB1W20SuWa(60Wa)	Briquets	1274	961	610	1148	0.38		(e)
107	9	AB1W20SuWa(60Wa)	Briquets	1472			1270	0.38		(e)
107R	9	AB1W20SuWa(60Wa)	Briquets	1481	544	526	1310	0.47		(e)
107RR	9	AB1W20SuWa(60Wa)	Briquets	1480	500	410	1306	0.28		(e)
107RRR	9	AB1W20SuWa(60Wa)	Briquets	1432	680	526	1284	0.33		(e)
107RRRR	9	AB1W20SuWa(60Wa)	Briquets	1485	762	662	1292	0.43		(e) (f)
107RRRRR	9	AB1W20SuWa(60Wa)	Briquets	1472	564	797	1391	0.25		(e)
108	9	AB1W20SuWa(60Wa)	Briquets	1472	-	-	1472	0.16		(e)
108R	9	AB1W20SuWa(60Wa)	Briquets	1490		572	1468	0.40		(e)
108RR	9	AB1W20SuWa(60Wa)	Briquets	1480	635	536	1426	1.00		(e)
94	9	AB1W20SuWa(60Wa)	Briquets	1472	482	582	1320	0.82		(e)

(a) Unless otherwise specified chlorine preheater was hot. Heat to R-1 turned off simultaneously with addition of chlorine.
For all "preheater" experiments, 11 inches of boric oxide-carbon briquets in hot zone, supported by carbon pellets in cold zone.
Bed height, R-1, was 11 inches for all experiments.

(b) Briquetted feed, except where noted.

(c) R-1 heated throughout.

(d) Volume of vent gas high (indicating reaction) because of high R-1 temperature.

(e) Gas furnace (R-1) and flue gas blower off.

(f) Acid briquets used in preheater instead of C-briquets.

TABLE XXI

RESULTS OF CHLORINATION WITH USE OF CHLORINE PREHEATER

Expt. No.	Exit Gas Vol. ft.^{3}	Exit Gas Stream Composition CO per cent	CO$_2$ per cent	O$_2$ per cent	Time Excess Cl_2 Observed hr. (a)	Remarks
BL-						
92	4.23	-	-	-		Shutdown due to leak on top or R-2
92R	2.31	8.1	0	19.1		
96	0.42	12.1	13.7	26.0		
99	1.91	-	-	-	0.16	Preheater heat off
TSR-						
*18	3.0	14.4	13.6	0.6	0.50	Preheater back on stream (no heat)
19	2.65	8	26.6	0.6	0.37	plug
20	4.58	36.7	26.1	3.0	0.40	
21	3.74	42	39.6	16.4		
22	3.53	28.8	21.1	1.7		Shutdown due to several plugs
23	5.50	25.2	15.6	1.6		
BL-						
101	0.85	-	-	-		Excess chlorine throughout experiment
						Plug in second condenser
102	1.48	4.8	26.6	3.2		Gas furnace off during experiment
103	1.84	13.6	50.0	2.4	0.33	
104	3.28	50.5	20.9	3.6	0.48	
103R	0.78	2.8	48.4	1.6		Gas and blower off
105	-	-	-	-	-	Shutdown due to plug in second condenser
105R	4.25	23.0	28.0	2.0		Condenser plugged
106R	0.78	No Orsat Reading			0.17	Shutdown plugs (c)
106RR	0.67	No Orsat Reading			0.47	Shutdown plugs (c)
107	-	No Orsat Reading			0.25	Shutdown plugs (c)
107R	0.53	No Orsat Reading				Shutdown due to several plugs (c)
107RR	1.02	No Orsat Reading				(c)
107RRR	0.42	No Orsat Reading			0.33	Plug in preheater (c)
(b)107RRRR	2.93	42.3	17.2	0	0.43	(c)
107RRRRR	0.71	No Orsat Reading				Preheater split open (c)
108	-	No Orsat Reading			0.10	(c)
108R	0.67	No Orsat Reading			1.10	(c)
108RR	1.70	No Orsat Reading			0.25	(c)
94	0.21	No Orsat Reading				Shutdown Preheater turned out (c)

(a) Elapsed time before excess chlorine appeared in effluent gas stream, as indicated by color change in potassium iodide solution.

(b) Acid briquets used in preheater instead of carbon briquets.

(c) Gas furnace and blower off.

TABLE [illegible]

OPERATING CONDITIONS FOR [illegible] OF ANHYDROUS [illegible]

Expt. No.	Feed to Reactor R-1	Feed to Reactor R-2	R-1 Feed	R-2 Feed	Bed Temperature R-1 °F	Bed Temperature R-2 °F	Duration of Expt. hr.	Time Before Plug hr.	Time of Excess Cl_2 Observed hr.	Remarks
BL										
175	9.0	2.5	Anhydrous Borax Pellets (50 per cent excess carbon)	A 1500 [illegible] 40 [illegible] Briquets	1510	1076	[illegible]	[illegible]	Not Observed	Plug in effluent gas line (e)
176	9.0	2.5	Anhydrous Borax Pellets (50 per cent excess carbon)	Carbon Briquets (e)	1070	1170	0.83	No Plug	Not Observed	Leak at reactor flange (d)
181	9.0	2.5	Anhydrous Borax Pellets (25 per cent excess carbon)	Same as BL 175 (e)	1000	1130	0.86	No Plug	0.25	
186	9.0	2.5	Anhydrous Borax Pellets (20 per cent excess carbon)	Same as BL 175 (e)	1300 1355 1320 1310	1305 1335 1007 1390	0.80	0.70	0.06	
187	9.0	2.5	Anhydrous Borax Pellets (50 per cent excess carbon)	Same as BL 175 (e)	1031 1166 1139	1072 1000 1335	0.96	No Plug	0.9	
188	9.0	2.5	Anhydrous Borax Pellets (50 per cent excess carbon)	Carbon Briquets	Start 1000 High 1250	1005	0.50	No Plug	0.44	Bed leak in R-1
189	9.0	2.5	Anhydrous Borax Pellets (50 per cent excess carbon)	Carbon Briquets	932 1101 1060	1373	0.95	No Plug	0.17	
190	9.0	2.5	Anhydrous Borax Pellets (50 per cent excess carbon)	Carbon Briquets	752 1202 964	1410 1307	0.95	No Plug	0.30	
191	20.0	7.2	Anhydrous Borax Pellets (50 per cent excess carbon)	Carbon Briquets	1626	1378	0.80	0.17		Plug in effluent gas lines.
194	9.0	0.0	Anhydrous Borax Pellets (50 per cent excess carbon) (f)	Al000 Granules 3.0" to 1.2" diameter	1590	199	0.65	0.13	Not Observed	Frequent shutdowns plugs in effluent gas lines
204	9.0	2.5	Anhydrous Borax Pellets (25 per cent excess carbon)	Carbon Briquets	1360	1391	1.50	0.83	1.05	Plug in effluent gas line during experiment (g)
206	9.0	2.5	Anhydrous Borax Pellets (25 per cent excess carbon)	Carbon Briquets	1468	1391	1.5	0.83	1.05	Plug in effluent gas line during experiment (g)
207	9.0	2.5	Anhydrous Borax Pellets (25 per cent excess carbon)	Carbon Briquets	1607 1589	1391 1391	0.75	0.75	Not Observed	Plug in effluent gas line (g)
208	9.0	2.5	Anhydrous Borax Pellets (25 per cent excess carbon)	Carbon Briquets	1418 1652 1832	1364	2.0	No Plug	1.0	No plugs but R-1 residue badly fused
209	9.0	2.5	Mixture of borax chunks + C-pellets (50 per cent excess carbon)	Carbon Briquets	1220 1067 1220	1427 1391 1427	3.49	No Plug	0.26	R-1 thermowell burned through
210	9.0	2.5	Mixture of borax chunks + C-pellets (50 per cent excess carbon)	Carbon Briquets	1202 1256 1256	1382 1373 1373		No Plug	0.25	R-1 thermowell burned through
216 (h)	9.0	2.5	Mixture of borax chunks + C-pellets (50 per cent excess carbon)	Carbon Pellets	1265 1324 1274	1382 1625	0.58	No Plug	0.25	Thermowell burned out - bottoms fused
217 (h)	9.0	2.5	Mixture of borax chunks + C-pellets (50 per cent excess carbon)	Carbon Pellets	1220 1409	1346 1440 1328	1.0	No Plug	0.58	

(a) Bed height for all experiments R-1, 11 inches, R-2, 24 inches.
(b) Borax used in all experiments. 11 inches of feed in hot zone (3 inches i.d. nickel pipe), supported by carbon pellets in cold zone.
(c) Elapsed time before chlorine appeared in effluent gas stream, as indicated by color change in potassium iodide solution.
(d) Actual composition of R-1 feed was found to be 173 per cent excess boron due to unaccountably severe carbon losses during sintering.
(e) Boric oxide-carbon briquettes erroneously charged.
(f) Incompletely calcined. (calcined at 900°F)
(g) System opened once for plug removal.
(h) Carbon monoxide fed to R-1 at 1.0 cu.ft./hr. at S.T.P.

179	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
180	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] [illegible] [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
183	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
184	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible] [illegible] [illegible] [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
185	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] [illegible] [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
186	[illegible]	82.1	0.02		89.70		22			66.6	12.0	2.0					
187	1.02	11.1	88.6	0.10	100.10	94.6	50	0.16	(i)	20.0	15.0	0	82.5	91.0	5.0	5.0	20.6
188	0.49	5.0	94.1		100.19	70.5	12	0.07	(j) (k)	30.0 66.0	60.8 36.0	2.0 6.0	15.0	71.1	1.2	1.3	11.6
191	0.16	50.6	30.1	0.6	90.06	115	731	[illegible]	1.07	No Orsat Analysis					66.0	20.6	
196	[illegible]	89.0	0.80	0.22	99.10	30.3	225	[illegible]	0.66	23.6	12.6	0.0	92.0	65.0	10.0	10.6	47.6
204	0.02	77.9	11.7	0.46	97.72	131	291	0.02					59.1	72.9	20.6	33.0	19.5
206	0.80	86.7	5.2	0.4	98.0	162	812	1.22	5.66	60.9	0.2	12.6	71.2	72.6	72.3	66.4	77.6
20	9.63	89.0	0.25	0.0	98.68	70	605	1.19	6.01	33.0 18.0	17.2 15.2	6.6 2.4	70.9	76.0	56.0	66.6	57.6
208	9.22	88.6	1.61	0.4	99.35	161	676	0.70	12.65(l)	0	10.2	16.0	70.3	51.1	63.2	29.0	31.0
209	0.16	3.1	94.5	0.1	97.79	-	9.4		3.69	0.4 0 0	0 0 0	11.6 6.6 10.0	19.5		0.1		[illegible]
210	0.35	4.2	94.0	0.1	98.50	152	27	0.05		0.8(m) 0(n)	0 0	6.4 2.4	52.1	19.9	2.0	2.9	7.1
216	No Product Formed					112	0	0									
217	0.42	6.9	90.5	-	97.82	106	16	0.35					71.1	49.1	1.5	2.1	4.6

(a) Includes Cl$^-$ from $COCl_2$. "Total per cent" is compensated.
(b) Boron trichloride recovered in condenser receivers and water scrubbers.
(c) B pass yield is B product/B charged.
(d) Cl$^-$ pass yield is Cl product/Cl charged.
(e) Overall B yield is B product/B charged minus unreacted Boron.
(f) Incorrect due to spent KOH solution in Orsat.
(g) Incomplete recovery of chlorine due to no analysis on carbon bed bottoms.
(h) Exceeds 100 per cent because boric oxide-carbon briquets were inadverdently charged to R-2.
(i) Temperature at R-1 = 1103°F.
(j) Temperature at R-1 = 1202°F.
(k) Temperature at R-1 = 966°F.
(l) Temperature at R-1 = 1418°F.
(m) Temperature at R-1 = 1202°F.
(n) Temperature at R-1 = 1256°F.

TABLE XXIV

CHLORINATION OF BORIC OXIDE VERSUS BORAX (a)

	Description of Process	Expt. No. BL-	Boron Pass Yield per cent	Boron Overall Yield per cent	Boron Recovery per cent	Chlorine Pass (b) Yield per cent	Chlorine Recovery per cent	$\frac{HCl}{BCl_3}$	Temperature °F (f)	BCl_3 Production Rate lb./hr. (c)
I	$B_2O_3 \cdot C$ Briquets	-	74	88	95	70	70.9	0.15	1300	1.41
II	$Na_2B_4O_7 \cdot C$									
	A. 50 per cent Excess Carbon (d)	191	64.4	-	-	28.6	-	0.16	1426	0.76
	B. 25 per cent Excess Carbon	(e)	48.9	60.3	71.9	38.7	68.2	0.27	1500(f)	0.99
	C. 50 per cent Excess Carbon (h)	187	5.6	20.0	82.5	5.9	91.4	1.65	932(g)	0.14
	D. 50 per cent Excess Carbon (h)	188	3.2	13.6	75.4	3.3	71.1	2.45	752(g)	0.07
	E. $Na_2B_4O_7$ Chunks + Carbon Pellets; (50 per cent Excess Carbon)	210	2.9	7.3	52.1	2.9	79.9	5.6	1250(g)	0.05
	F. NBO Chunks + Carbon Pellets (50 per cent Excess Carbon) with supplemental CO feed	217	1.5	4.6	71.1	2.1	49.1	6.6	1300(f)	0.35

(a) 24-inch carbon bed used in all experiments.
(b) Based on total chlorine fed to R-1 and R-2.
(c) Based on 90 cu.ft./hr. S.T.P. to R-1.
(d) For experiment BL-191 only.
(e) Average of experiments BL-204, 206, 207, and 208.
(f) Nominal temperature of bed.
(g) Start-up temperature of bed.
(h) Low temperature experiment.

TABLE XXV
EFFLUENT GAS STREAM COMPOSITION, BORAX VERSUS BORIC OXIDE

	$Na_2B_4O_7 \cdot C$ Feed BL-207	$B_2O_3 \cdot C$ Feed (Briquets) BL-143
Temperature, °F	R-1 1600	R-1 1312
Composition (per cent)	R-2 1390 (a)	R-2 1458 (a)
Inerts	26.6	24.5
CO	19.45	14.6
CO_2	10.10	5.1
O_2	2.76	1.0
BCl_3	25.10	34.9
Cl_2	0.36	2.3
$COCl_2$	0.00	0.04
HCl	15.70	17.7

a) 24-inch carbon bed

TABLE XXVI
OPERATING CONDITIONS FOR CHLORINATION OF BORON CARBIDE (a)

Expt. No. BL	Cl_2 Rate lb./hr. R-1	Cl_2 Rate lb./hr. R-2 (c)	R-1 Solid Feed (figures in per cent)		R-2 Solid Feed	Bed Temperature R-1 °F	Bed Temperature R-2 °F	Duration of Expt. hr.	Time Before Plug hr.	Remarks
158	9	[illegible]	Boron Carbide Batch 118 Briquets	17 83	No. 8-2	1550 1637		0.50	None	Thermowell burned out
[illegible]	9		Boron Carbide Batch 118 Briquets	17 83	No. 8-2	1477 1637		0.32	None	Excess Cl_2 at .133 hr.
160	9.0		Boron Carbide C Pellets	17 83	No. 8-2	1256		0.72	None	
161	9	3	Boron Carbide C Pellets	17 83	No. 8-2	1225		0.75	None	Excess Cl_2 at .20 hr.
[illegible]	9	1.0	B_4C Lot No. 1 C Pellets	33.3 66.6	P.F. Carbon Briquets	1210	1465	0.50	None	Thermowell burned out
[illegible]	9	1.0	B_4C Lot No. 1 C Pellets	33.3 66.6	P.F. Carbon Briquets	1210 (1000)	1500	0.33	None	Thermowell burned out
[illegible]	[illegible]	1.0	B_4C Lot No. 1 C Pellets	27.5 72.5	P.F. Carbon Briquets	1130	1409	0.83	None	Excess Cl_2 at .25 hr
[illegible]	[illegible]	1.5	B_4C Lot No. 1 C Pellets	22.5 77.5	P.F. Carbon Briquets	1216	1332	0.60	None	Excess Cl_2 at .416 hr.
180	[illegible]	1.0	B_4C Lot No. 2 C Pellets	24 76	P.F.A. Briquets A 150W25.8 SuWa (68.9Wa)	1078	Room Temperature	0.66	None	
181	[illegible]	1.0	B_4C Lot No. 2 C Pellets	24 76	P.F. Briquets A 150W25.8 SuWa (68.9Wa)	1157	Room Temperature	0.50	None	Excess Cl_2 at .10 hr.
182	9.0	1.0	B_4C Lot No. 2 C Pellets	25 75	P.F. Briquets A-150W25.8 SuWa (68.9Wa)	1158	Room Temperature	0.32	None	
189	9.0		B_4C Carbon Powder	27.0 73.0		1436		1.0	None	Burned out thermowell, R-1
190	9.0		B_4C Carbon Powder	27.0 73.0		1564		0.55	None	Burned out thermowell
213	15.0	4.5	A100W-20SuWa (60Wa) Tablets + 5 per cent B_4C		C-Briquets	1202 1364 1364	1382 1373 1373	0.42	None	Reactor thermowell burned out
214	13.0	3.9	A100W-20SuWa (60Wa) Tablets + 5 per cent B_4C		C Briquets	1202 1693 1693	1319 1292 1292	0.50	None	Reactor thermowell burned out
215	9.0	2.7	A100W-20SuWa (60Wa) Tablets + 5 per cent B_4C		C-Briquets	1211 1314 1067	1382	0.58	None	
222	20.	0	Ba No. RC-210 2016, BA + 20 lb. C + 113 g. B_4C		Resintered A300WSuWa Briquets	1250	Room Temperature	.217	.183	Heat off during experiment Shutdown because of plug in reactor bed

(a) R-1 bed height, 11 inches for all experiments.
R-2 bed height, 24 inches, except BL-189 and 190 which had no R-2 bed.

(b) Heat was turned off simultaneously with introduction of chlorine, except for BL-158 and 159 where external heat was maintained for the duration of the experiment.

(c) Chlorine rate to R-1 varied in attempt to maintain and control reactor bed temperature.

TABLE XXVII
RESULTS OF CHLORINATION OF BORON CARBIDE

Expt. No.	Analysis of Product Condensed: B per cent	Cl⁻ (a) per cent	Cl_2 per cent	$COCl_2$ per cent	Total per cent	HCl Made g.	BCl_3 Made g. (b)	BCl_3 production Rate lb./hr.	Volume ft³	Vent Gas Analysis: CO per cent	CO_2 per cent	O_2 per cent	Recovery: B per cent	Cl_2 per cent	Pass Yield: B (c) per cent	Cl (d) per cent	Overall Yield (e) B per cent
BL-																	
158	8.43	81.50	9.28	-	99.21	49.5	120	1.20	4.59	7.6	12.4	[illegible]	47.11	42.10	26.11	19.07	33.16
159	8.33	81.16	10.58	-	100.07	44.3	109.3	.80	3.53	12.8	13.6	10.4	21.56	36.26	17.70	16.90	18.56
160	1.72	17.1	73.5	< .05	92.33	41.1	91.8	.31	.520	7.6	24.8	6.8	(f)	83.1	(f)	21.1	(f)
161	3.64	35.8	58.4	< .05	97.85	43.0	161.1	.48	.212	0	1.0	2.0	(f)	70.2	(f)	31.1	(f)
175	9.20	90.2	0.18	0	99.58	41.6	296	1.12	.92	14.5	(g)	7.5	75.1	59.5	19.0	51.0	62.0
176	9.21	89.3	0.18	0	98.69	66.5	196	1.31	.39	46.0	(g)	4.0	73.0	80.0	13.3	59.2	33.3
177	Product Not Analysed				-	-	-	-	.85	16.0	(g)	14.0	-	-	-	-	-
179	9.10	88.5	0.46	0	98.06	90.2	476	1.75	.63	No Orsat Analysis			66.6	99.1	60.[illegible]	80.5	54.0
180	Product Not Analyzed				-	-	-		.18	No Orsat Analysis			-	-	-		-
181	.09	2.17	96.8	0	99.06	71.[illegible]	2.27	.01	.03	No Orsat Analysis			75.6	81.9	0.64	2.16	1.50
182	.03	2.57	99.6	0.1	102.23	21.9	2.91	.02	.32	No Orsat Analysis			63.1	70.6	0.22	2.12	0.20
189	Sample Card Misplaced			0	-	7.9	549	1.21	.17	No Orsat Analysis			-	-	-		
190	7.04	68.6	21.6	0	97.24	9.9	382	1.53		No Orsat Analysis			[illegible].0	103.6	28.0	77.1	51.0
213	9.45	88.6	0.26	0.0	98.31	56	518	2.72	(h)	0	2.0	0.8	56.5	72	33.2	61.5	51.0
214	9.54	89.9	0.19	0.0	99.63	8	581	2.56	(h)	0.4	11.6	3.6	94.5	[illegible]	43.6	56.5	82.[illegible]
215	9.18	89.5	0.36	-	99.04	4	158	0.6	-	-	-	-	69.6	36.1	13.0	21.5	30.0
222	8.21	73.9	17.8	0.84	100.15	48	192.4	1.96		-			60.0	71.0	9.1	66.0	51.0

(a) Includes Cl from $COCl_2$

(b) BCl_3 recovered in condenser receivers and water scrubber

(c) B pass yield = B product/B charged

(d) Cl⁻ pass yield = Cl product/Cl charged

(e) Overall B yield = B product/B charged minus unreacted B

(f) Reactor Bottoms Sample Misplaced

(g) In error due to use of spent KOH solution

(h) Wet test meter not working

TABLE XXVIII
CHLORINATION OF BORIC OXIDE VERSUS BORON CARBIDE

Description of Process	Expt. No. BL-	Operating Conditions: R-1 Heated During Expt.	Operating Conditions: C-Bed Used	Boron: Pass Yield per cent	Boron: Overall Yield per cent	Boron: Recovery per cent	Chlorine (a): Pass Yield per cent	Chlorine (a): Recovery per cent	BCl_3 (b) Production Rate lb/hr.	$\frac{B \text{ in } BCl_3}{B \text{ white solids}}$	$\frac{HCl}{BCl_3}$ Wt. Ratio	Condensed Product Impurities: Cl_2 per cent	Condensed Product Impurities: $COCl_2$ per cent
BOC Briquet Experiments													
1. $B_2O_3 \cdot C$; No C-Bed	-	Yes	No	44	72	78	62	83.3	1.24	8.5	0.11	6-27	0.0 to 0.9
2. $B_2O_3 \cdot C$; 24 in. C-Bed	-	Yes	Yes	74	88	95	70	79	1.43	89	0.15	0.07 to 7.9	0
B_4C Experiments													
1. Mixture of 1/4-1/2 in. chunks B_4C, Mixed with C-Pellets	158 and 159	Yes	No	22	26	34	37	40	1.0	148	0.41	10.	-
2. Same as 1	160 and 161	No	No	(d)	(d)	(d)	26	77	0.40	125	0.36	66.	0.05
3. Same as 1; Cl_2 Rate Varied	179	No	Yes	40.7	56.4	66.6	80.5	80.5 99.3	1.02	(c)	0.19	0.46	0
4. $(B_4C + C)$ coarse powder	190	No	No	29	52	77	77	104	1.53	-	0.026	21.6	0
5. $B_2O_3 \cdot C$ Pellets with 5 per cent B_4C (mixed together)	213	No	Yes	33	52	77	62	72	1.63	(c)	0.11	0.26	0

(a) Based on Total chlorine fed (R-1 and R-2)
(b) Based on 9.0 cu.ft./hr. S.T.P. to R-1
(c) Not presented: value would be very high
(d) Sample misplaced

TABLE XX.X

OPERATING CONDITIONS FOR CHLORINATION WITH USE OF SUPPLEMENTAL OXYGEN (a)

Expt. No. BL-	Cl_2 Rate to R-1 cu.ft.at.S.T.P.	Cl_2 Rate to R-2 cu.ft.at.S.T.P.	Solid Feed R-1 (b)	Solid Feed R-2	Bed Temperature R-1 °F	Bed Temperature R-2 °F	Duration of Expt. hr.	Time of Plug hr.	Time Excess Cl_2 Observed hr. (c)	Remarks
218	9.0	0 (O_2 to R-1 .45 SCFH)	A100W Granules (1/8-1/4 in. D)	A150W25SuWa (70Wa) briquets	1292 1454 1022	No Heat	1.0	No Plug	.25	No "oxide", no fusion
219	9.0	0 (O_2 to R-1 .9 SCFH)	A100W Granules (1/8-1/4 in. D)	A150W25SuWa (70Wa) briquets	1247 1350 975	No Heat	1.0	No Plug	.067	No "oxide", no fusion
221	9.0	0 (O_2 to R-1 1.35 SCFH)	A100W Granules (1/8-1/4 in. D)	A150W25SuWa (70Wa) briquets	1247 1408 932	No Heat	1.0	No Plug	.15	No "oxide", no fusion

(a) Bed height: R-1, 11 inches, R-2, 24 inches.
(b) All experiments: 11 inches of feed in hot zone (contained in a 3 in. i.d. nickel pipe) supported by boric oxide-carbon briquets in cold zone.
(c) Elapsed time before chlorine first appeared in effluent gas stream as indicated by color change of potassium iodide solution.

TABLE XXX
RESULTS OF CHLORINATION WITH USE OF SUPPLEMENTAL OXYGEN

Expt. No. BL-	Analysis of Product Condensed: B per cent	Cl (a) per cent	Cl_2 per cent	$COCl_2$ per cent	Total per cent	HCl Made g.	BCl_3 Made g. (b)	BCl_3 Production Rate lb./hr.	Volume ft.^{3}	Vent Gas Analysis: CO per cent	CO_2 per cent	O_2 per cent	Recovery: B per cent	Cl_2 per cent	Pass Yield: B (c) per cent	Cl^- (d) per cent	Overall Yield (e): B per cent	per cent
218	3.90	38.4	56.1	-	98.4	76	263	0.58	-	-	-	-	102.[illegible]	[illegible]	34.1	20.6	73.0	
219	4.58	47.6	44.3	-	96.48	74	163	0.36	-	-	-	-	90.5	48.[illegible]	21.4	19.6	100.1	
221	4.95	50.5	41.2	-	96.65	83	349	0.77	-	29.2	4.2	4.8	97.1	68.4	63.[illegible]	60.[illegible]	70.[illegible]	

(a) Includes chlorine from phosgene
(b) BCl_3 recovered in condenser receivers and water scrubber
(c) B pass yield is B product/B charged
(d) Cl^- pass yield is Cl^- product/Cl_2 charged
(e) Overall B yields is B product/B charged minus unreacted B

TABLE XXXI

OPERATING CONDITIONS FOR ROTARY CHLORINATION EXPERIMENTS

Expt. No. RC-	Feed Formulation	Feed Analysis B per cent	Feed Analysis C per cent	Feed Analysis H per cent	Chlorinator Slope in./ft.	Retort Tube r.p.m.	Average Solids Feed Rate g./min.	Length of Line-out Period hr.	Duration of Expt. hr.	Average Chlorine fed during the Expt. cu.ft./hr. at S.T.P.	Total Chlorine fed during Expt. mole	Temperature in Reaction Zone °F	Total Liquid Product Condensed mole	Remarks
1	A100W granules, sintered	13.3	54.6	-	0.27	0.97	41	-	1.065	15.6	1480	1280	165	Numerous leaks and frequent plugging of glass wool filter plug in gas discharge line caused shutdown of the experiment.
2	A100W granules, sintered	13.9	-	0.405	0.28	1.0	65 (b)	-	0.55	15.6	760	-	0	Flights inserted-holes in end of chlorine inlet pipe plugged causing shutdown of the experiment. There were leaks and frequent plugging of the glass wool filter.
3	A100W granules, sintered	12.8	54.4	0.46	0.28	1.0	61.9	-	1.35	15.6	1880	-	0	Flights inserted. Fewer leaks than in previous experiments. Still some plugging of lines.
4	Sintered Powder made from sintered A100W granules	15.5	48.1	0.40	0.28	5.0	12.5	0.984 (c)	1.29	18.6 (a)	2000 (a)	-	477	Flights inserted-using chlorine preheater (inlet gas temperature was approximately 300°F). Very few leaks. Plug at chlorine inlet caused shutdown.
1 5	Same as RC-4	14.9	49.9	0.36	0.28	4.0	10.7	0.317	1.87	25.2 (a)	4200 (a)	-	1200	Stopped experiment because product receivers were full. Smooth operation. No detected leaks. Used no initial line-out period running gas directly to the caustic scrubber.
2	Same as RC-4	14.9	49.9	0.36	0.28	4.0	10.7	0	1.73	9.8 (a)	1520 (a)	-	1060	Plug in chlorine inlet line caused shutdown.
6	Same as RC-4	14.6	51.4	0.54	0.28	4.0	10.5	0.184	2.03	13.6 (a)	2460 (a)	-	1226	Plug in chlorine inlet caused shutdown.

(a) Figures do not include line-out period

(b) Based on a calibration made before the experiment

(c) For experiment 4 this figure is the length of time that chlorine was fed before liquid started to condense

TABLE XXXII

RECOVERIES AND YIELDS FOR ROTARY CHLORINATION EXPERIMENTS

Expt. No. RC-	Liquid Product from Condensers: Wt. mole	B per cent	Cl per cent	Cl_2 per cent	$COCl_2$ per cent	Uncondensable Gases, Water Scrubber: Wt. mole	B per cent	Cl per cent	HCl g./min.	Caustic: Wt. g.	B per cent	Cl per cent	BCl_3 Production Rate(a) lb./hr.	Conversion of Cl_2 per cent	Recovery of Cl_2 per cent	HCl Production Rate as BCl_3 (f) lb./hr.
1	165	3.83	40.1	52.9	1.8	No water scrubber				2566	0.02	8.57	0.297	4.9	25.0(b)	
2	0	-	-	-	-	No water scrubber				9025	0.01	1.67	-	-	19.7(b)	-
3	0	-	-	-	-	No water scrubber				7954	0.01	7.22	-	-	41.0	
4	677	3.44	37.0	49.0	1.6	4529	0.05	16.6	5.72(c)	10963	0.055	5.99	0.508	12.5	60.4(d)	0.909
-1	3200	1.24	13.4	84.6	0.6	(e) 3024 3265	0.02 <0.01	2.82 8.46	4.6 (e) 2.54	12135	0.01	5.88	0.507	9.3	81.5(d)	0.359
-2	1060	1.83	21.0	76.7	0.73	3073	0.01	4.10	1.28				0.267	12.6		0.181
6	1226	6.50	64.9	27.2	-	(e) 3094 3 88	0.06 0.18	3.83 13.9	9.28(e) 3.68	13310	<0.01	2.47	1.009	14.7	71.8(d)	0.521

(a) Based on boron in the liquid product and in the scrubbers.
(b) Figures do not include chloride in solid bottoms.
(c) Only one water scrubber used during lineout and run periods.
(d) Figure is for entire period of operation, line out and run.
(e) Line out period.
(f) Represents the amount of boron trichloride that could have reacted to form hydrogen chloride.

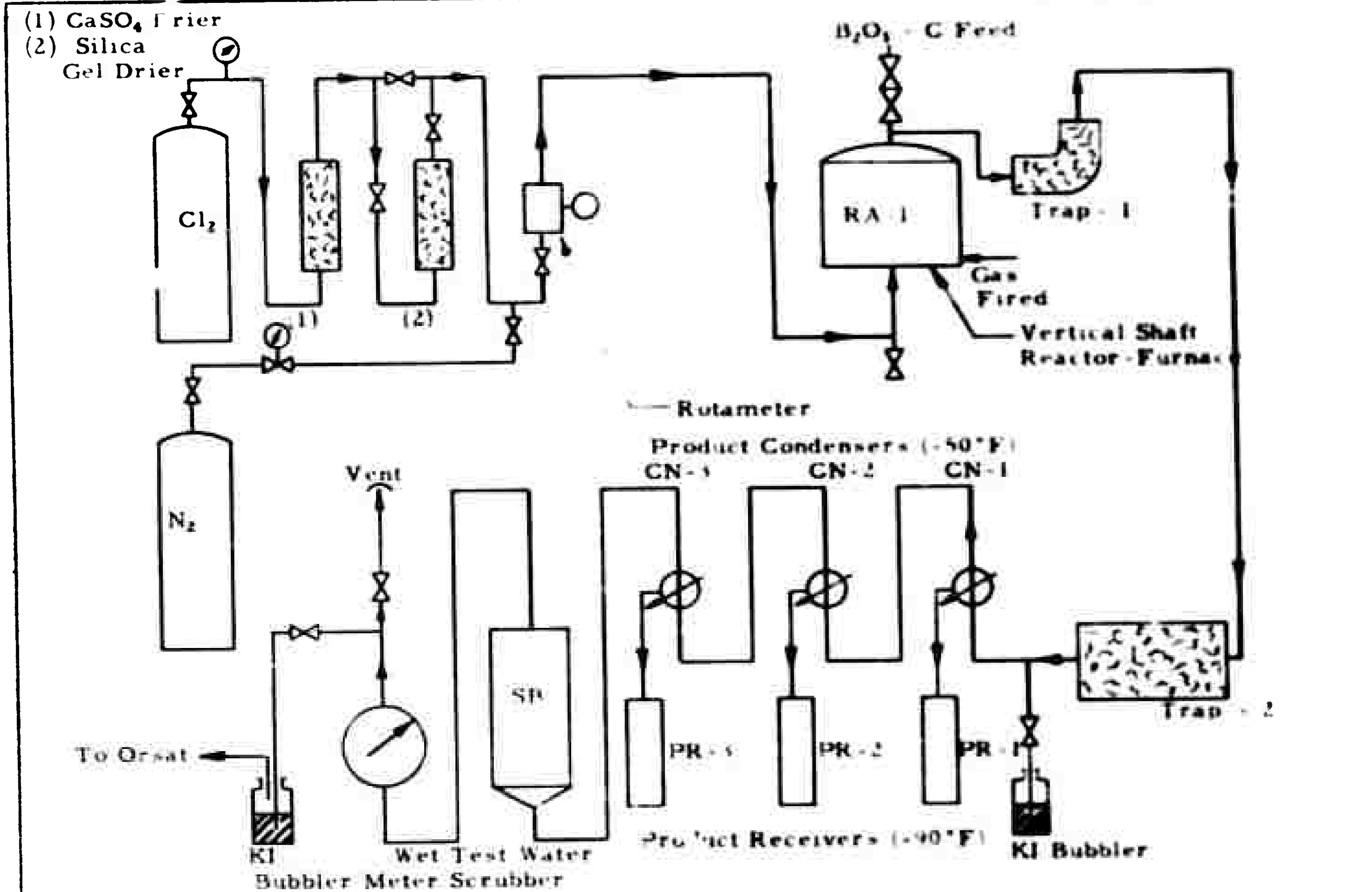
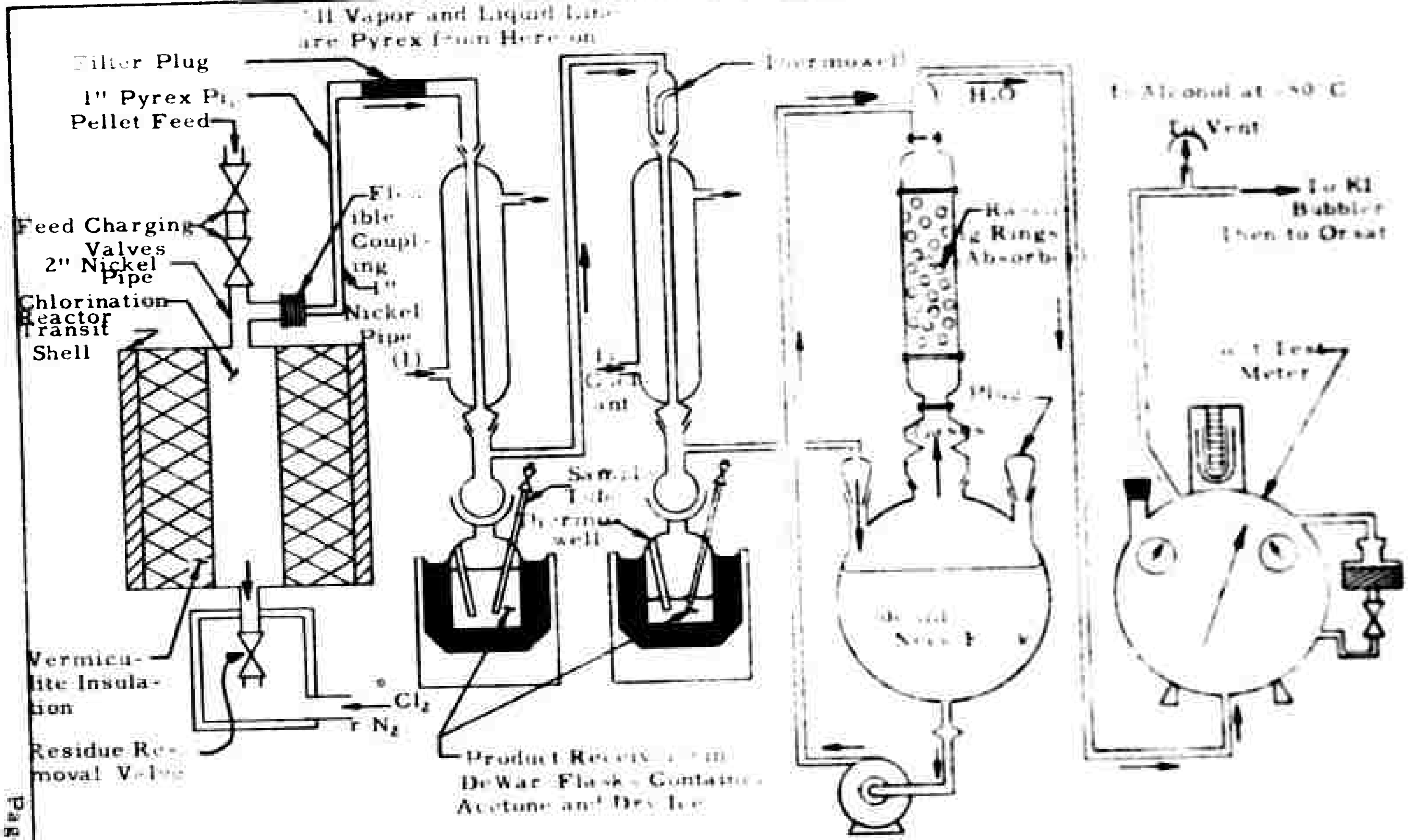


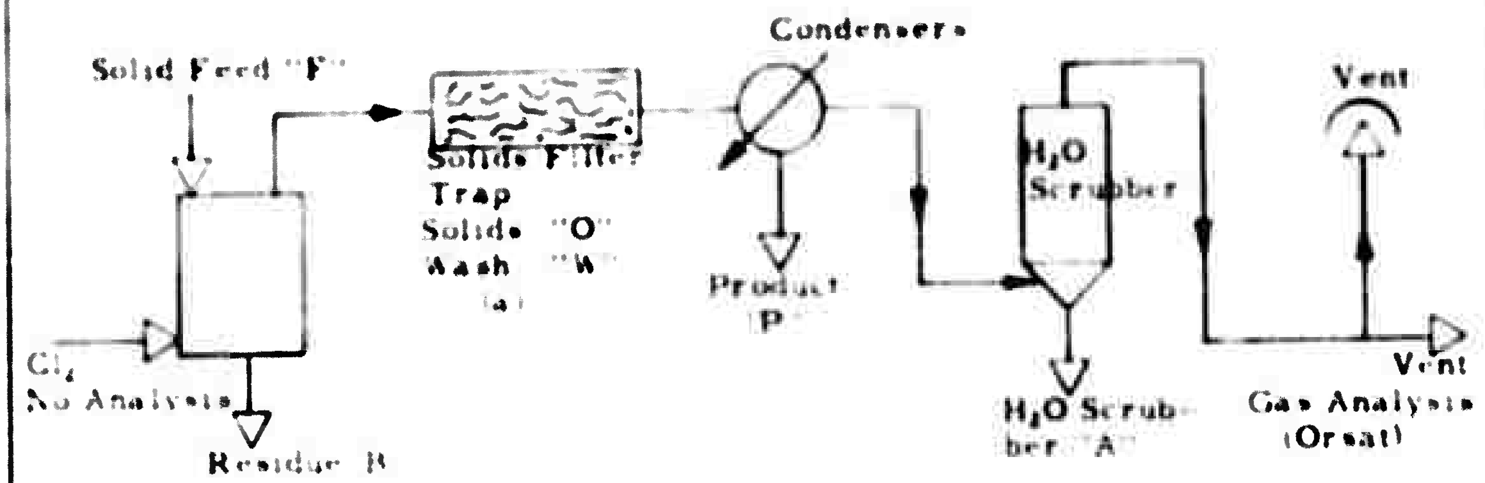
FIGURE 1 - PROCESS FLOW DIAGRAM LABORATORY SCALE BORON TRICHLORIDE APPARATUS. BASIC COMPONENTS

Note: Gas lines down stream from RA-1 are pyrex glass.



* From Drying Component

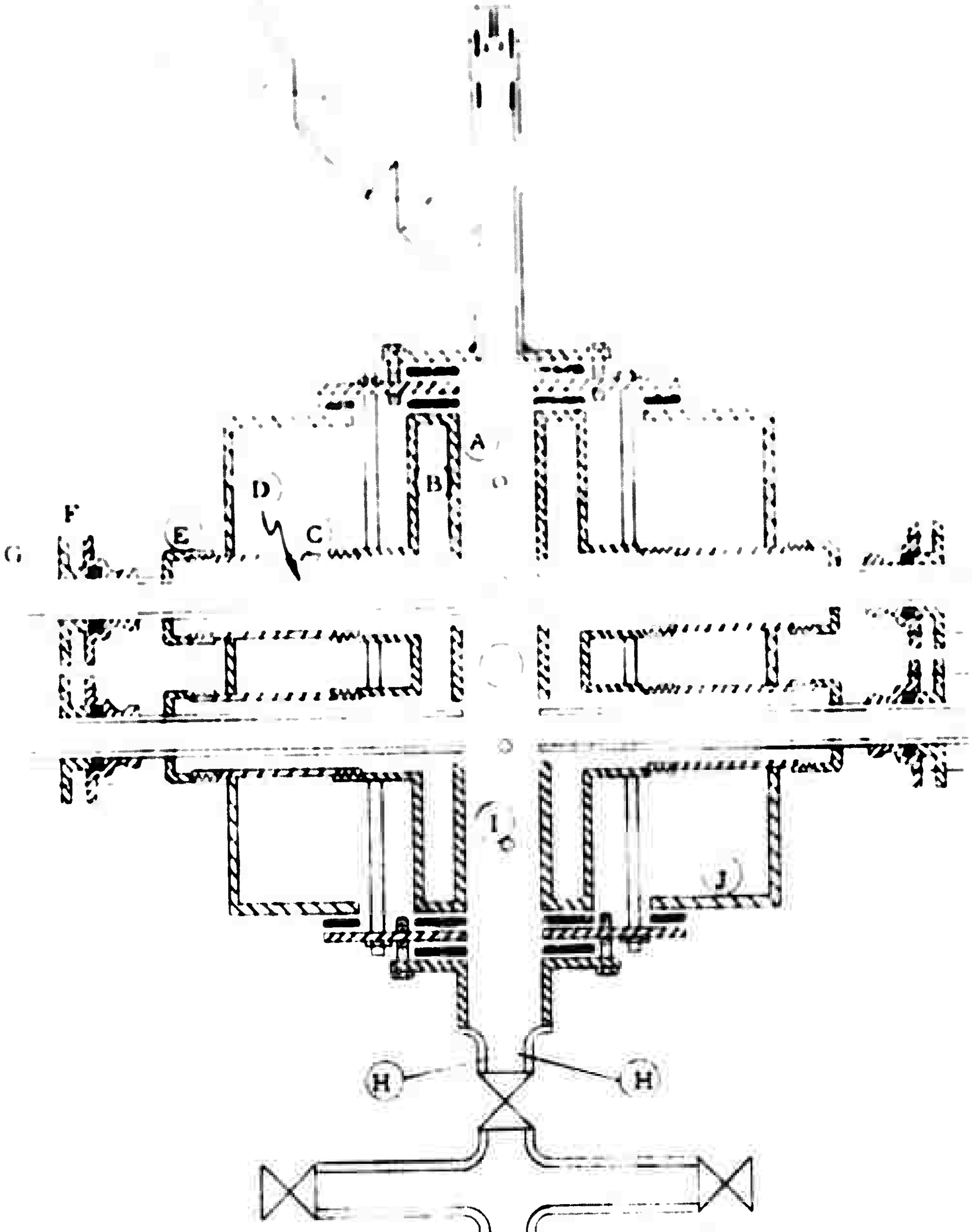
FIGURE 2 - PROCESS FLOW DIAGRAM ... SCALE BOR... TRICHLORIDE APPARATUS ... ASIC ... ENTS



Sample or Stream	Physical State	ANALYSIS									
		B	C	Cl^-	Cl_2	$COCl_2$	H	CO	CO_2	O_2	Other
Chlorine	Gas		No Analysis								
"F"	Solid (pellets, etc)	X	X				X				
"B"	Solid	X	X	(b)			(b)				
"O"	Solid	X	(b)	X	(b)						(c)
"W"	Liquid	X	(b)	X							(c)
"P"	(d)	X		X	X	X					
"A"	Liquid			X (e)							(c)
Vent Gas								X	X	X	

(a) Wash down of overhead lines at end of experiment
(b) Occasional Analysis
(c) Also Ni and Fe for some samples
(d) Liquid when sampled; gaseous at room temperature
(e) Total Cl^- : (includes Cl^- from emtal chloride formed by action of HCl on scrubber pump).

FIGURE 3 - CHEMICAL ANALYSES FOR CHLORINATION EXPERIMENTS



(A) Vycor or Ceramic Reactor Tube

(B) 4" SS Furnace Jacket Lined with sheet Nickel, 12" long

(C) 1-1/2" SS Electrode Jacket

(D) 27 mm. Vycor Electrode Sleev

(E) Packing Gland, SS-Vycor

(F) Packing Gland, Pyrex-Graphite Electrode

(G) Graphite Electrode

(H) 1/4" SS Tube Cl_2 Inlet

(I) 4 Thermowells

(J) Transite Box, 19" x 19" 12" Filled with Vermiculite

FIGURE 4 - BORON TRICHLORIDE ELECTRODE FURNACE REACTOR

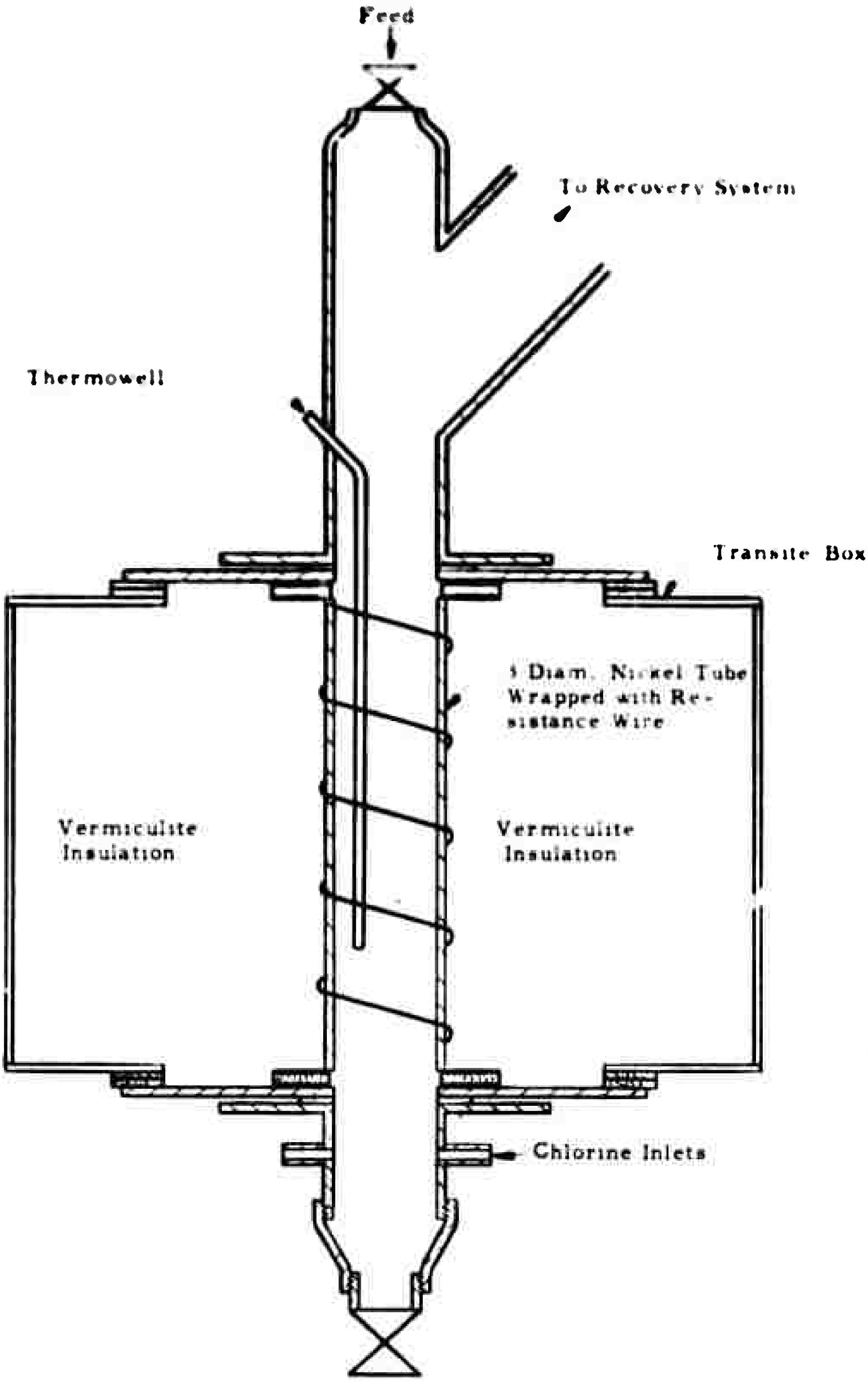


FIGURE 5 - EXTERNALLY REACTED ELECTRIC FURNACE

Figure 73

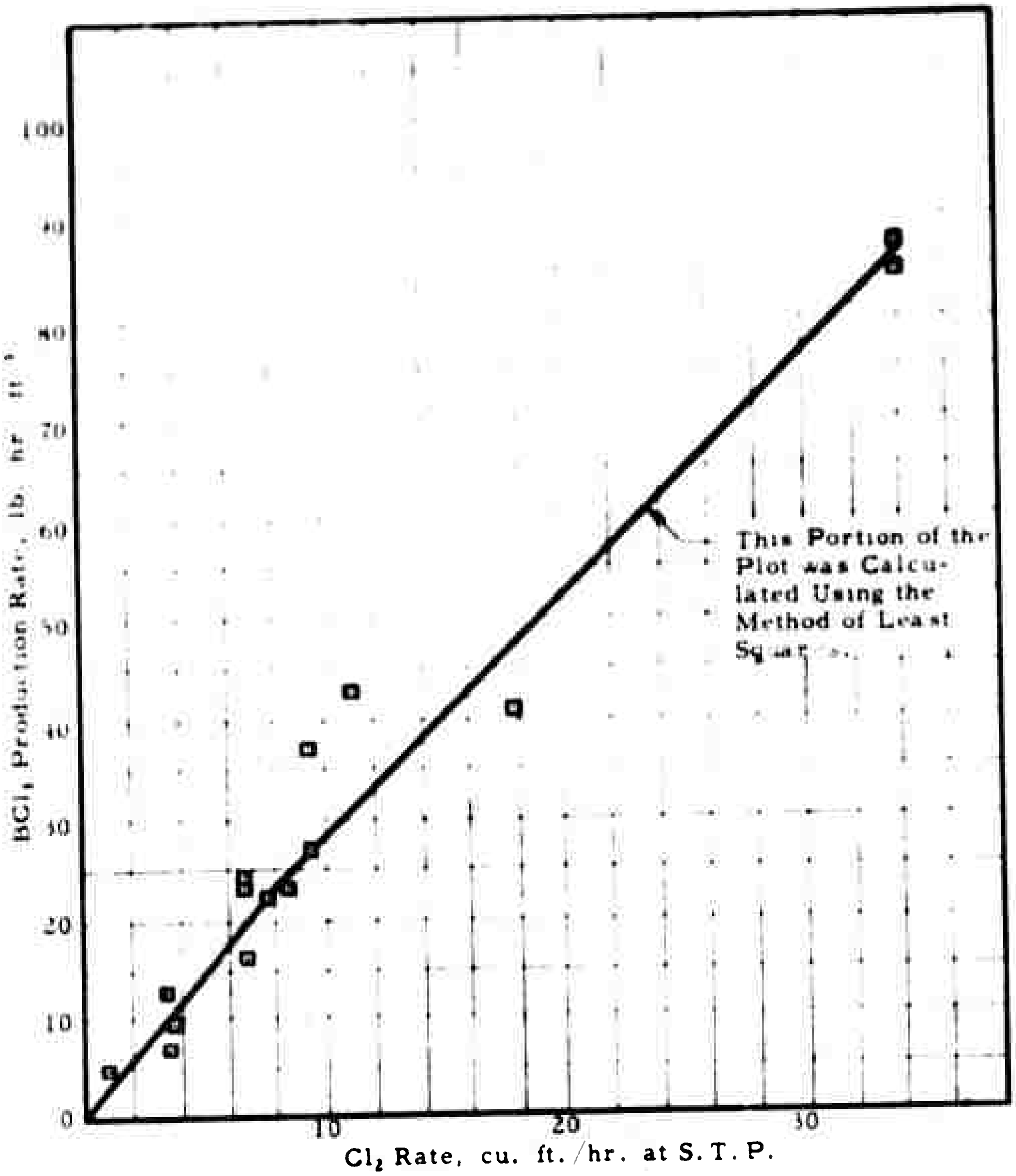


FIGURE 6 - PRODUCTION RATE versus CHLORINE RATE FOR BL EXPERIMENTS (BORIC OXIDE CARBON FEED FULL BED LEVEL)

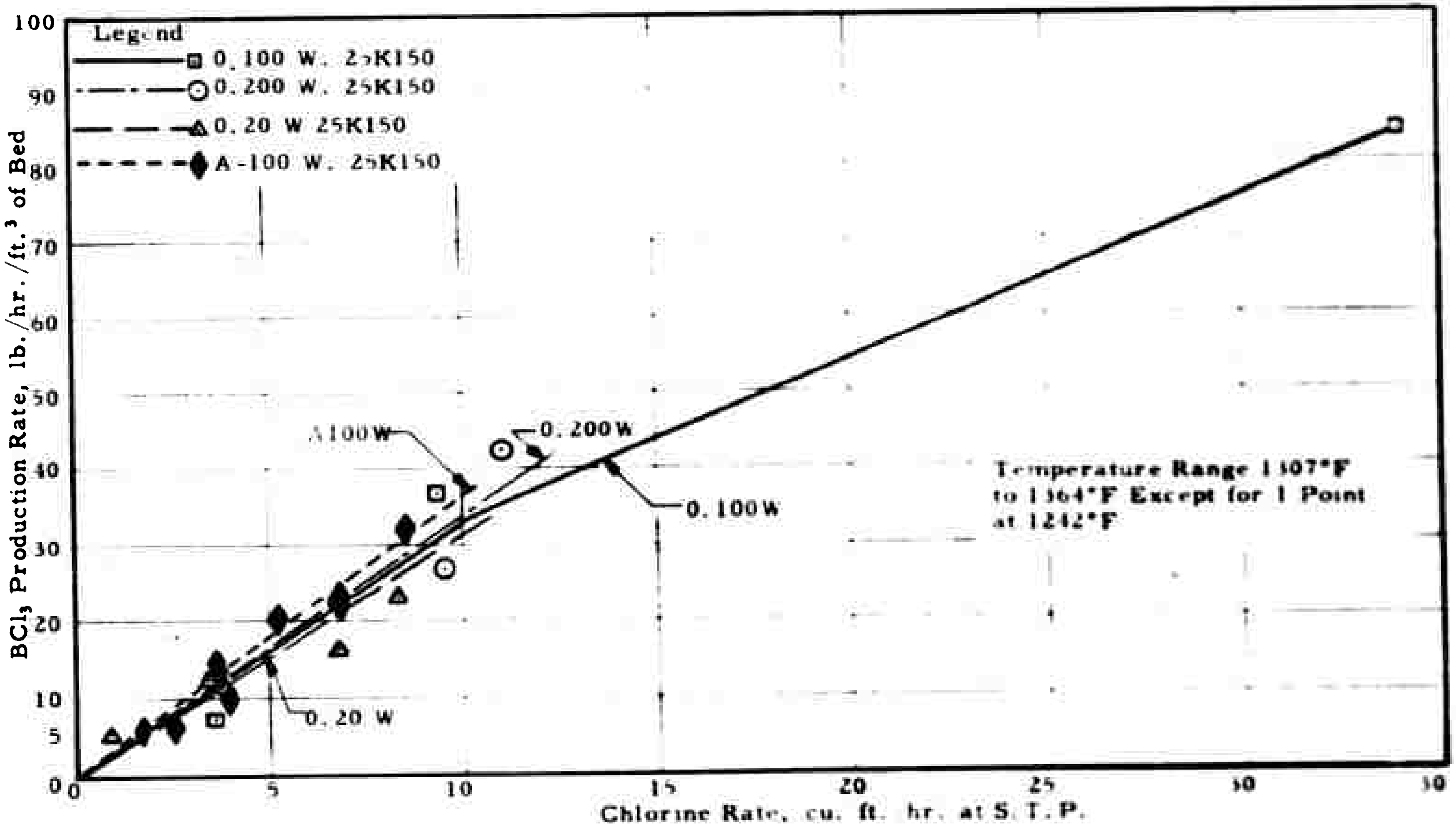


FIGURE 7 - EFFECT OF PELLET FEED FORMULATION ON BORON TRICHLORIDE PRODUCTION RATE VERSUS CHLORINE RATE FOR FULL BED EXPERIMENTS

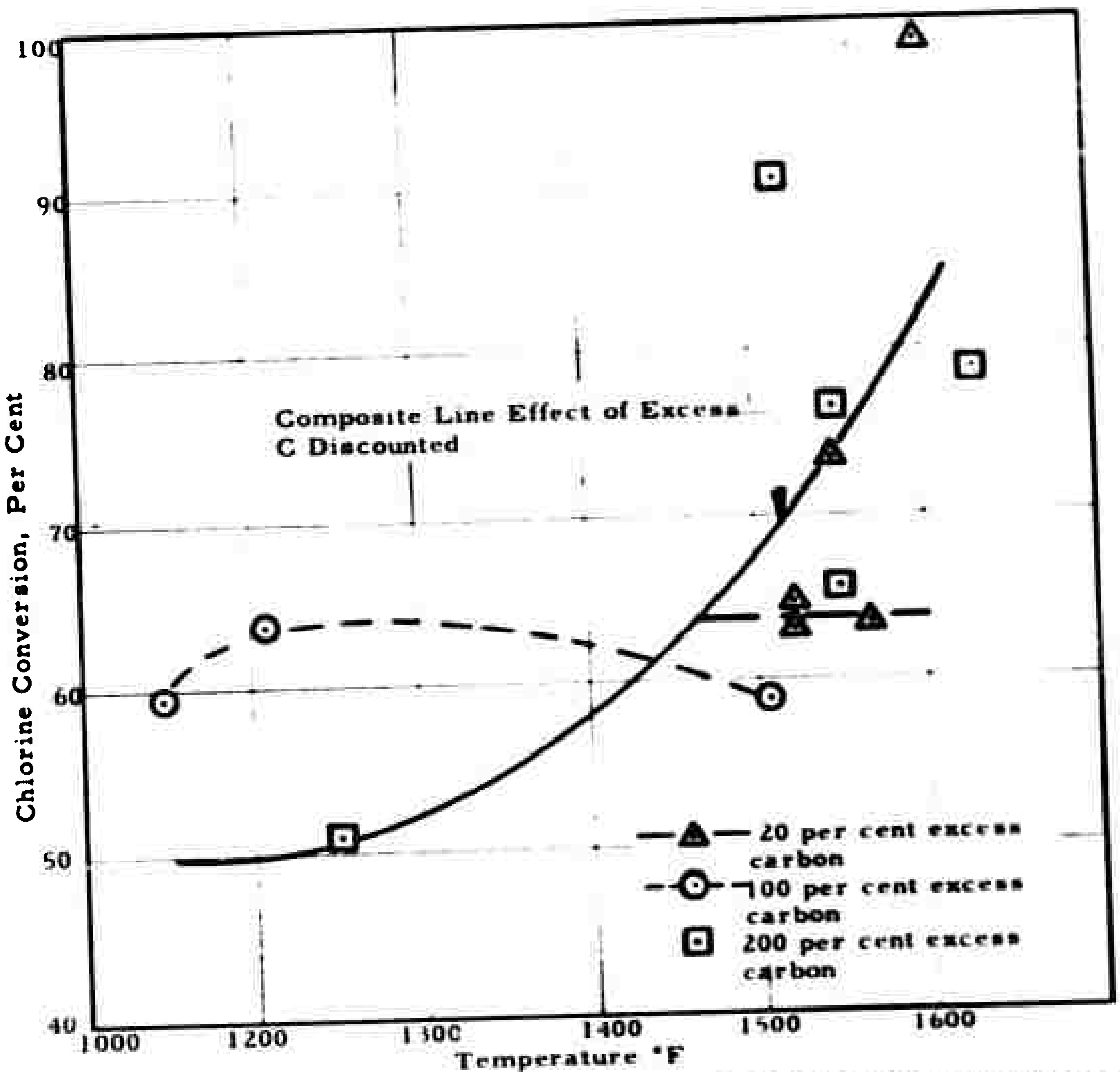


FIGURE 8 - EFFECT OF EXCESS CARBON ON CHLORINE CONVERSION VERSUS REACTOR TEMPERATURE

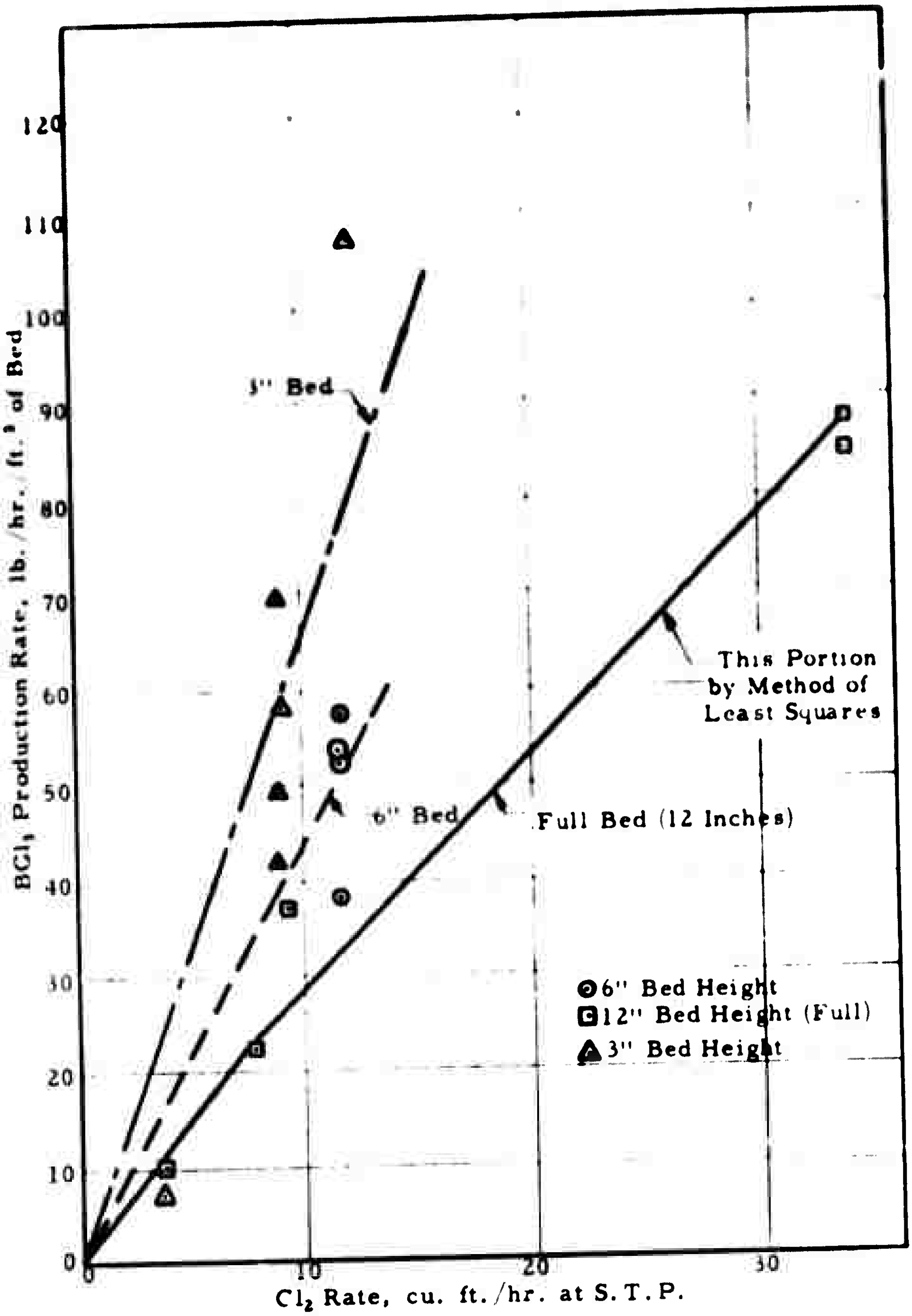


FIGURE 9 - BORON TRICHLORIDE PRODUCTION RATE VERSUS CHLORINE RATE FOR 3-, 6-, and 12-INCH BED HEIGHTS

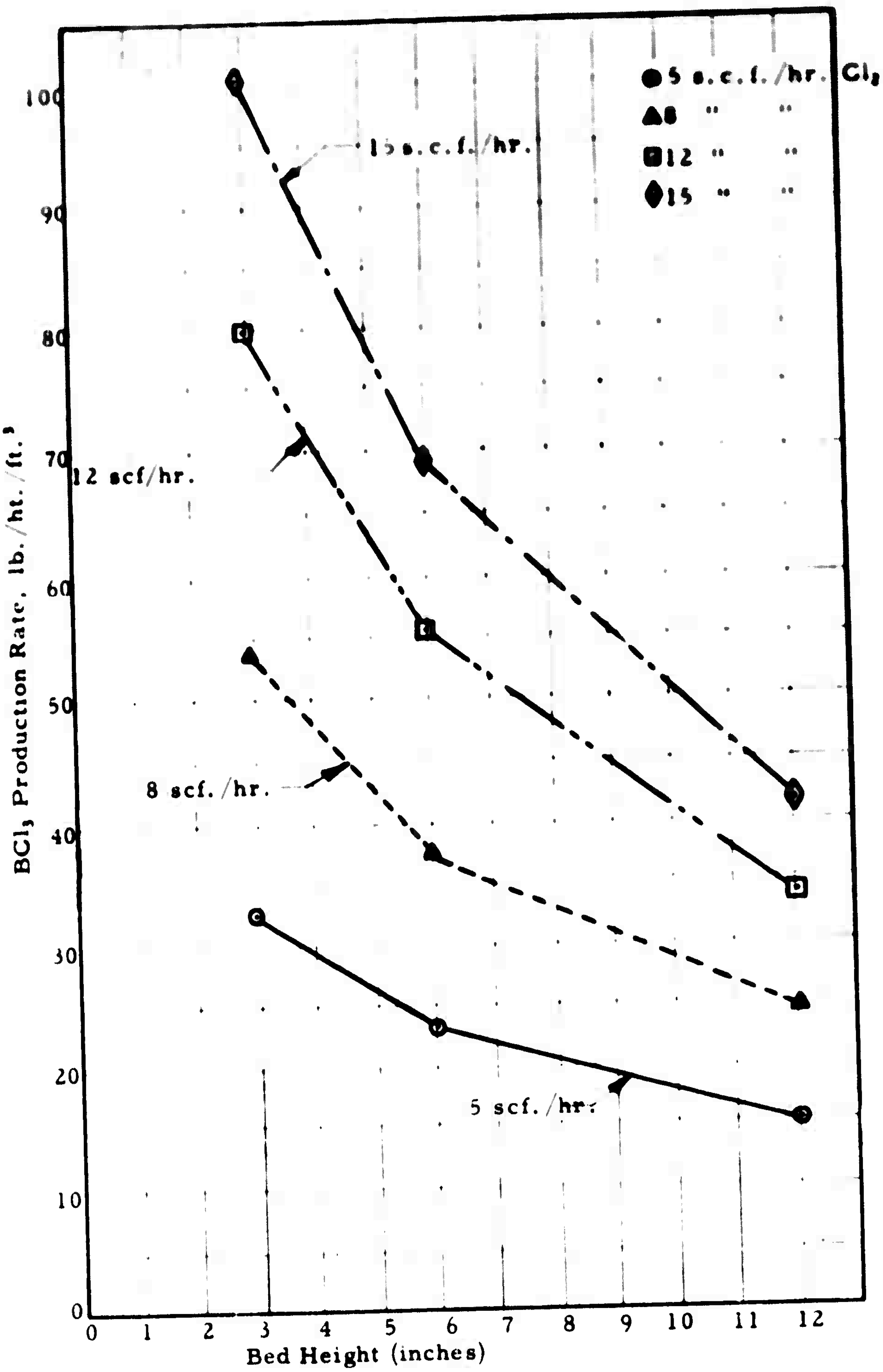


FIGURE 10 - EFFECT OF CHLORINE FEED ON BORON TRICHLORIDE PRODUCTION RATE VERSUS BED HEIGHTS

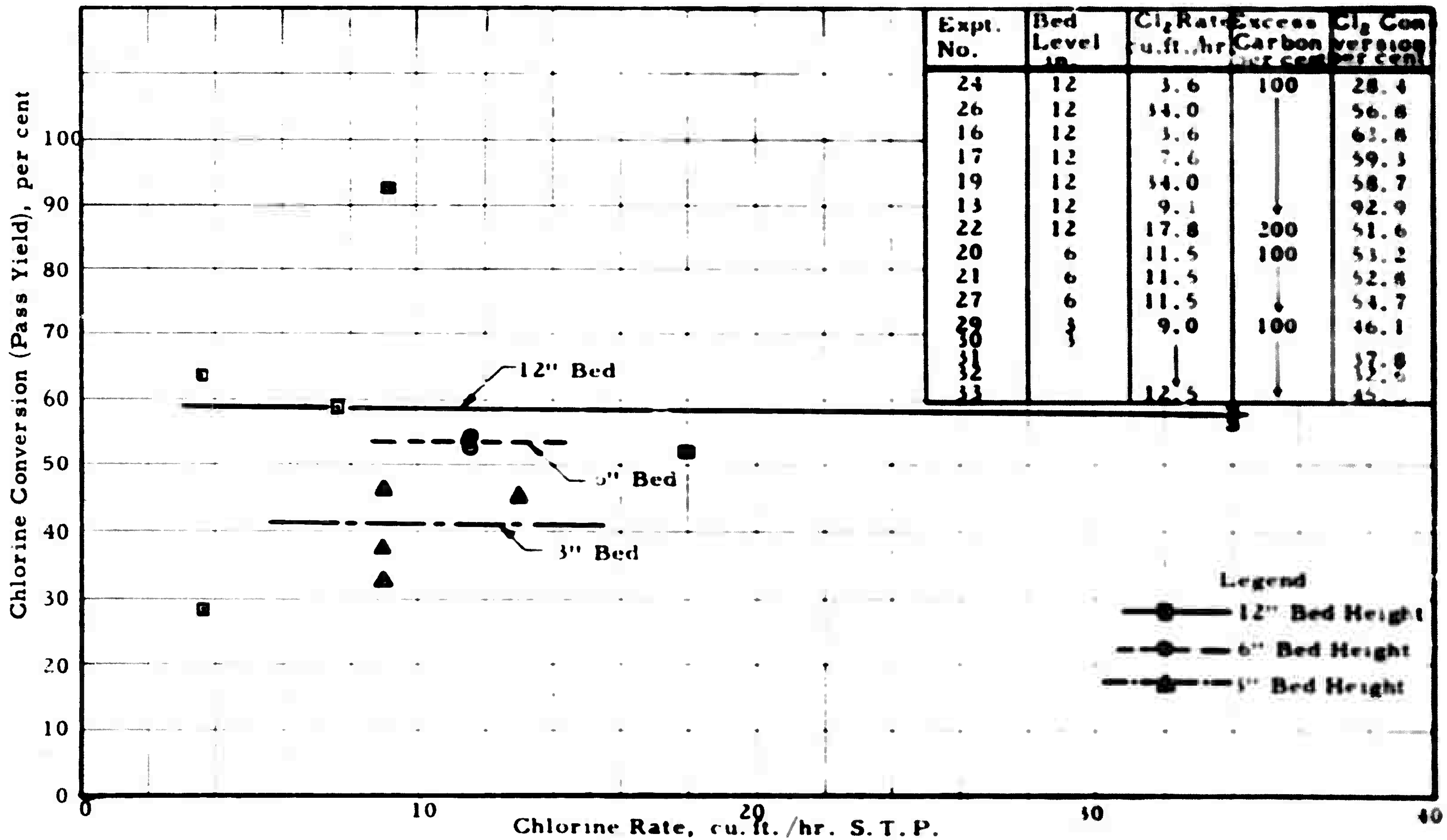


FIGURE 11 - CHLORINE CONVERSION VERSUS CHLORINE RATE FOR 3-, 6-, and 9-INCH BED HEIGHTS

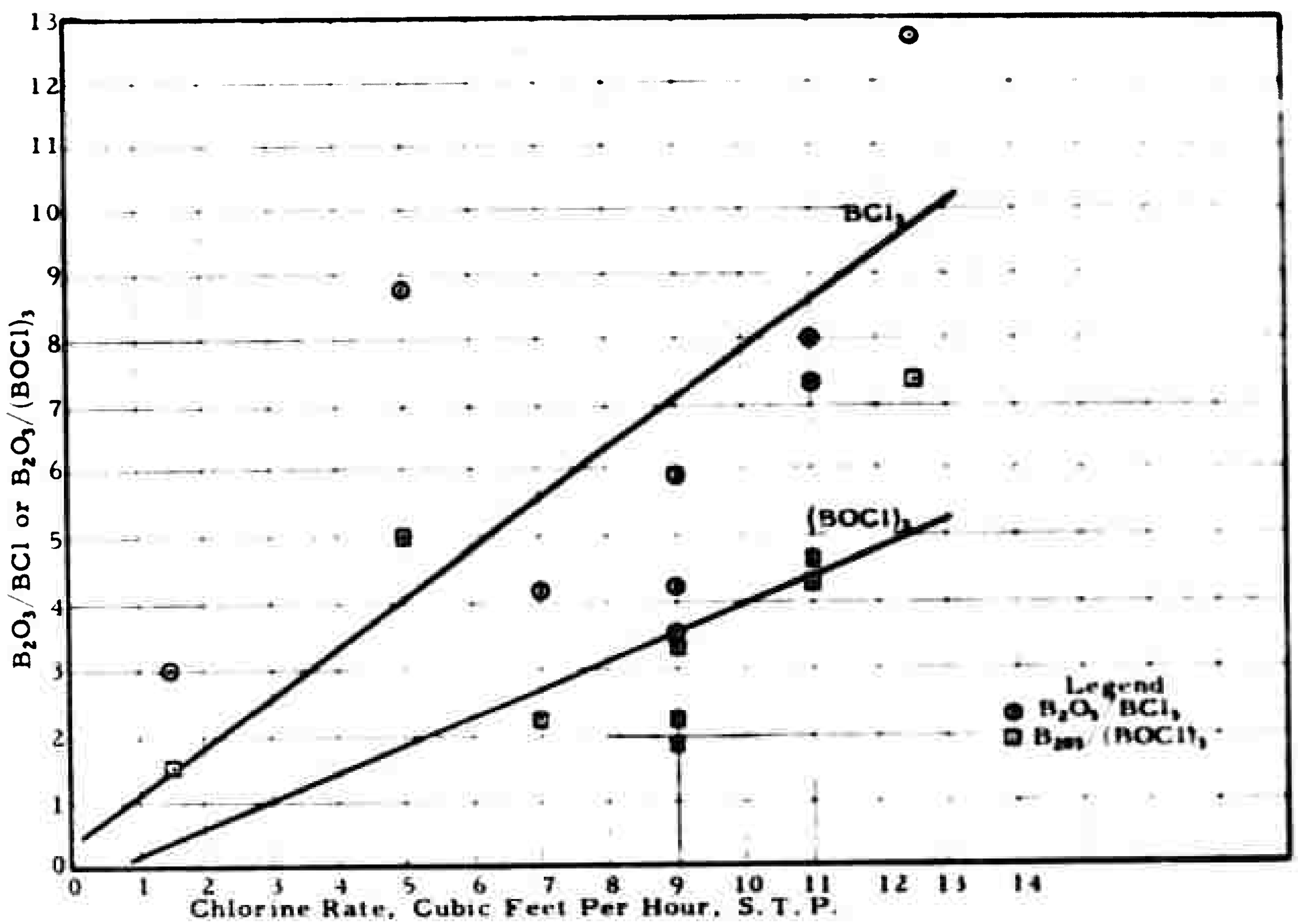


FIGURE 12 - BORIC OXIDE COMBINED WITH BORON TRICHLORIDE OR TRICHLORO-BOROXOLE IN GAS EFFLUENT FROM REACTOR

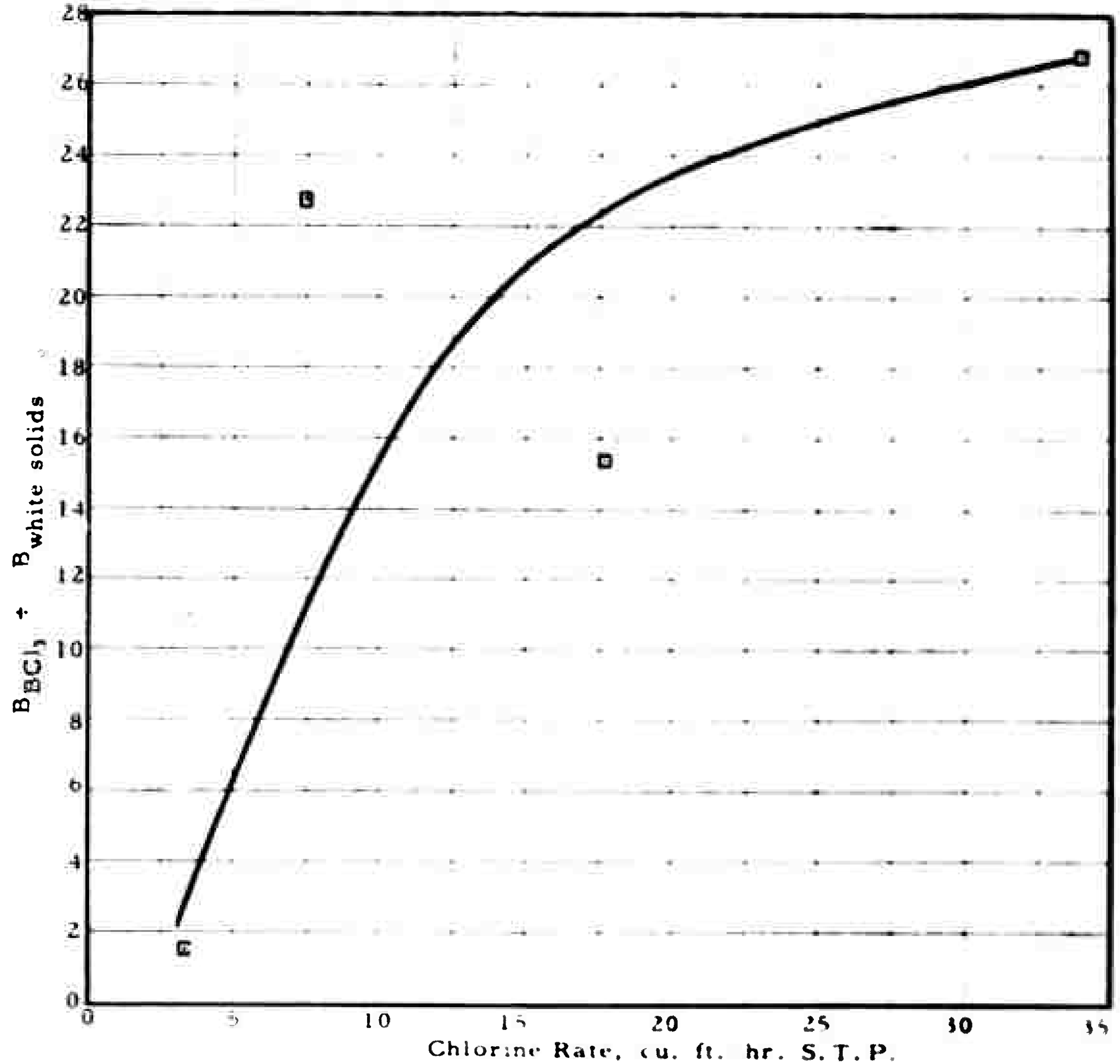


FIGURE 13 - EFFECT OF CHLORINE RATE ON BORON$_{BCl_3}$ to BORON$_{White\ Solids}$
RATIO FOR FLUID BED EXPERIMENT

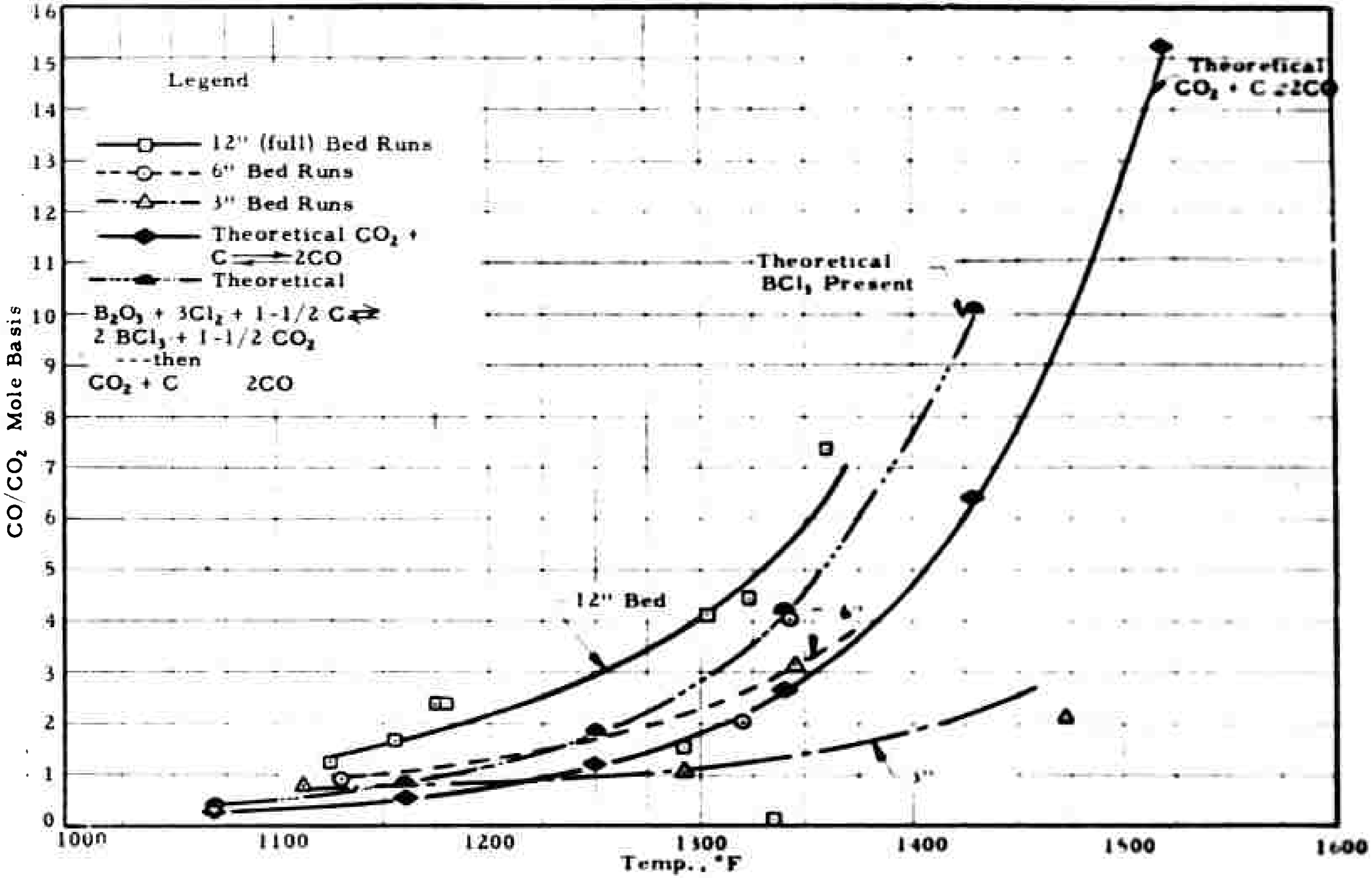


FIGURE 14 - EFFECT OF BED HEIGHT AND TEMPERATURE ON CARBON MONOXIDE TO CARBON DIOXIDE RATIO

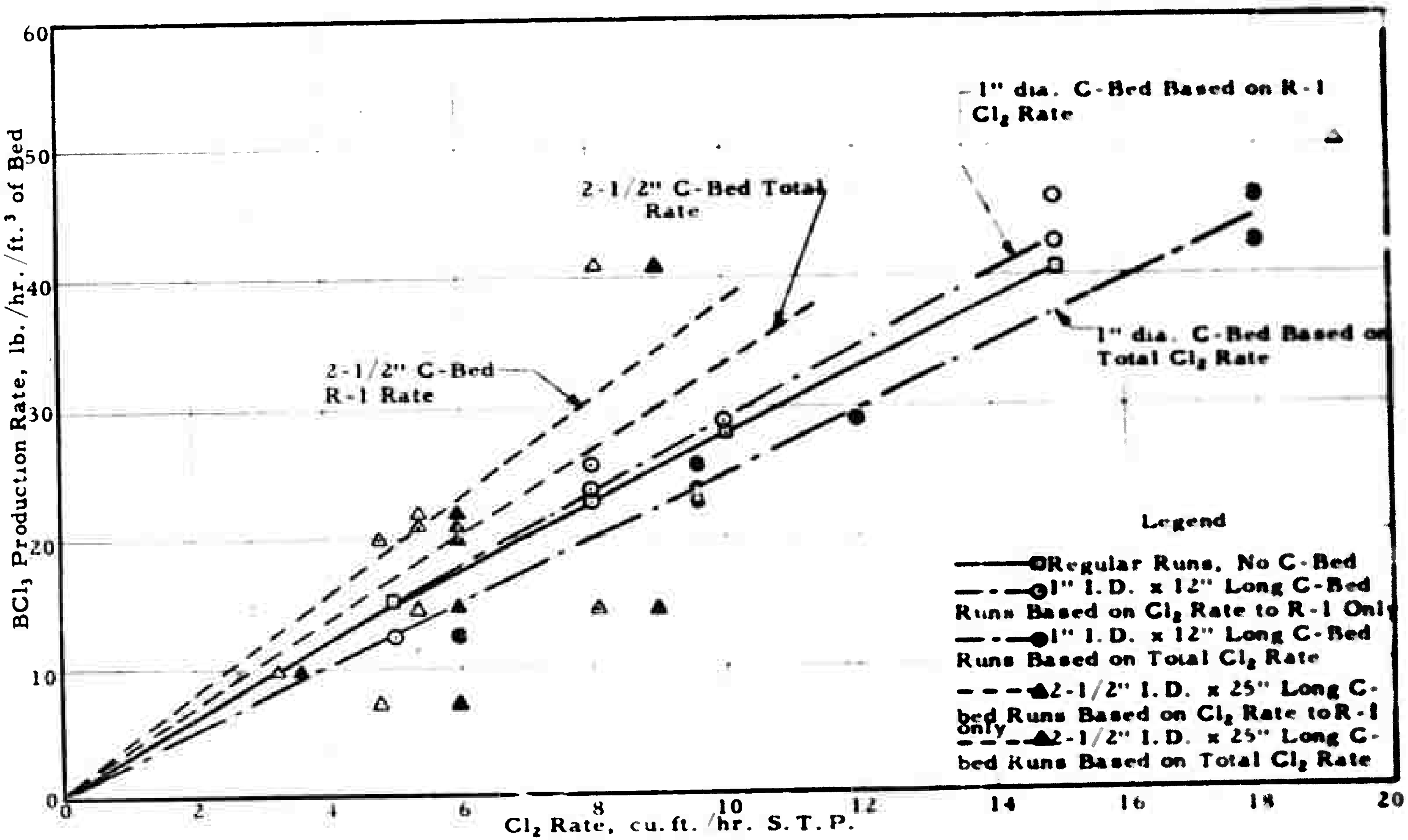


FIGURE 15 - EFFECT OF CARBON BED SIZE ON CHLORINE RATE VERSUS PRODUCTION RATE
(Horizontal Carbon Bed Experiments Only)

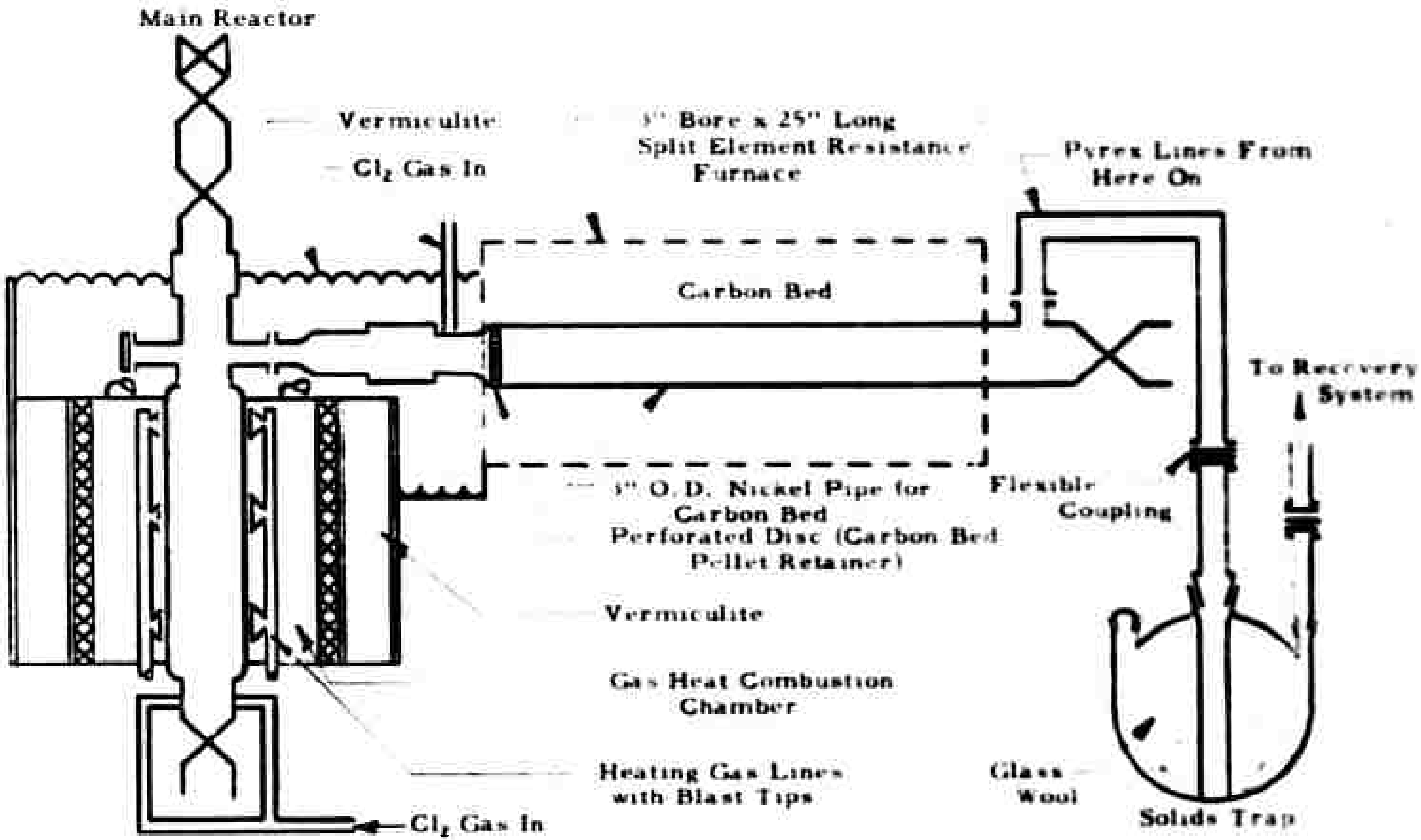


FIGURE 16 - REACTION CARBON BED AND SOLIDS RECOVERY APPARATUS FOR 25-INCH LONG HORIZONTAL CARBON BED EXPERIMENT

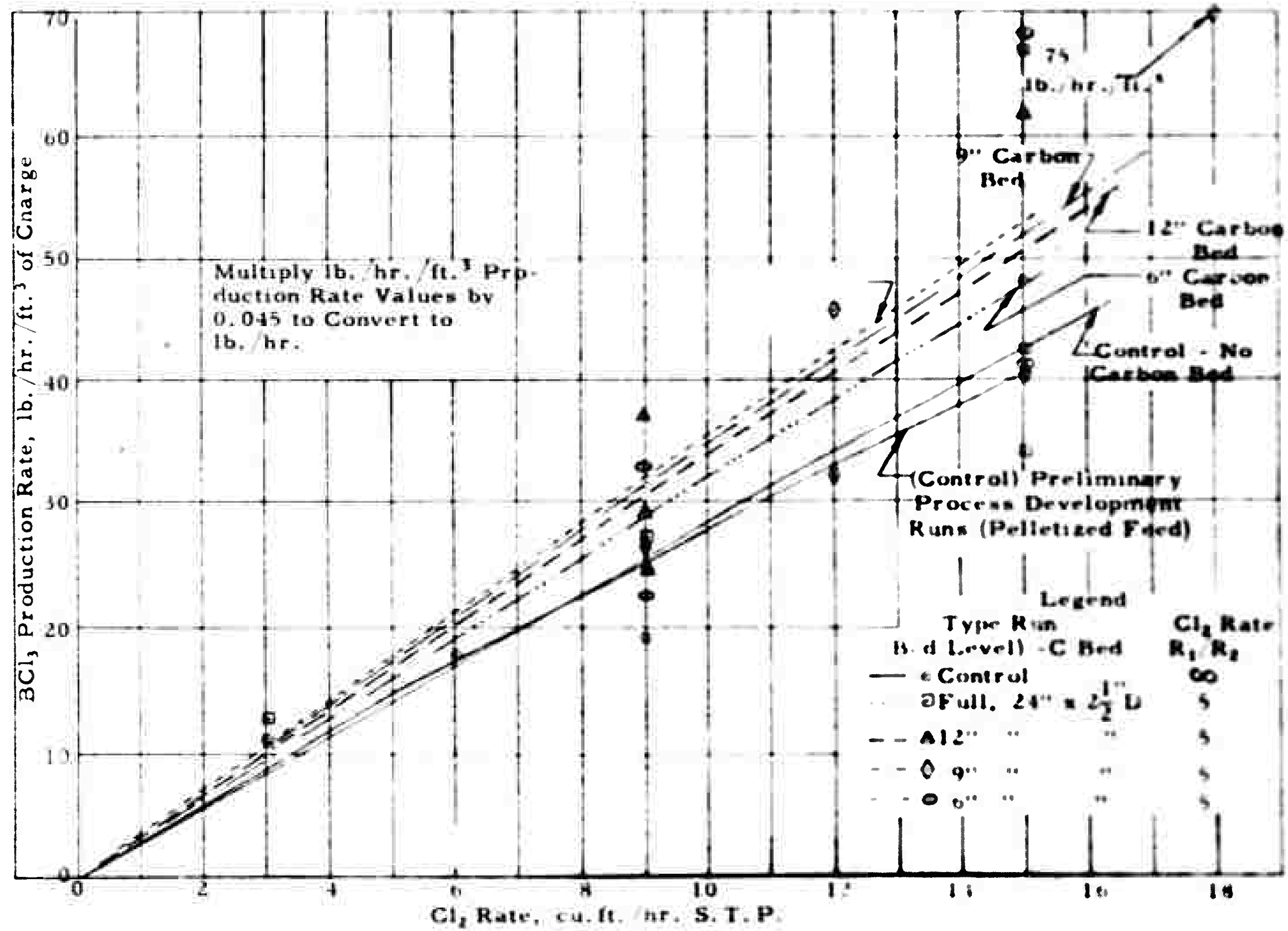


FIGURE 17 - EFFECT OF CARBON BED HEIGHT ON BORON TRICHLORIDE PRODUCTION RATE VERSUS CHLORINE RATE

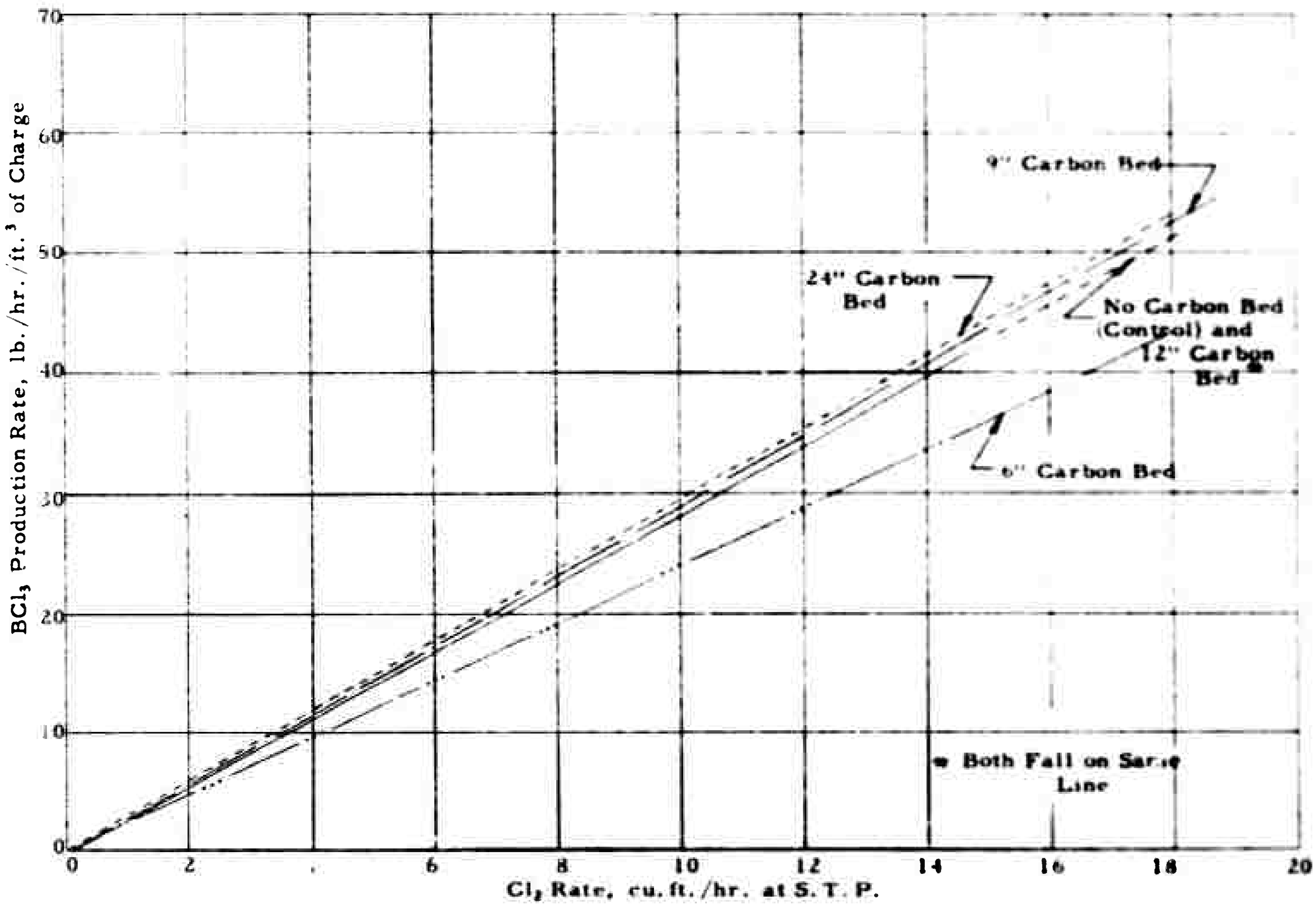


FIGURE 18 - EFFECT OF CARBON BED HEIGHT ON BORON TRICHLORIDE PRODUCTION RATE VERSUS CHLORINE RATE
(Based on Total Chlorine Rate)

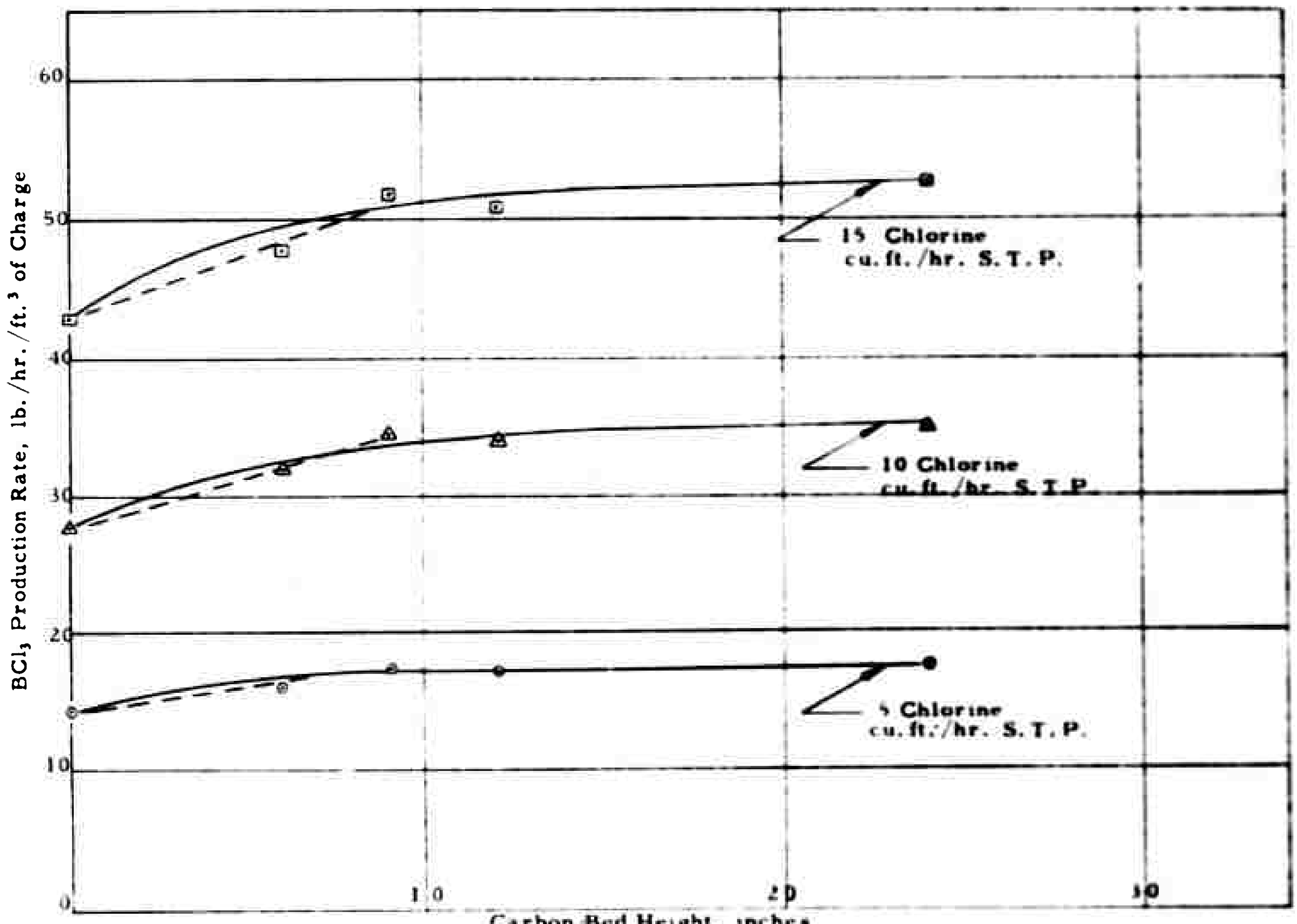


FIGURE 19. PRODUCTION RATE VERSUS CARBON BED HEIGHT AT VARIOUS CHLORINE RATES

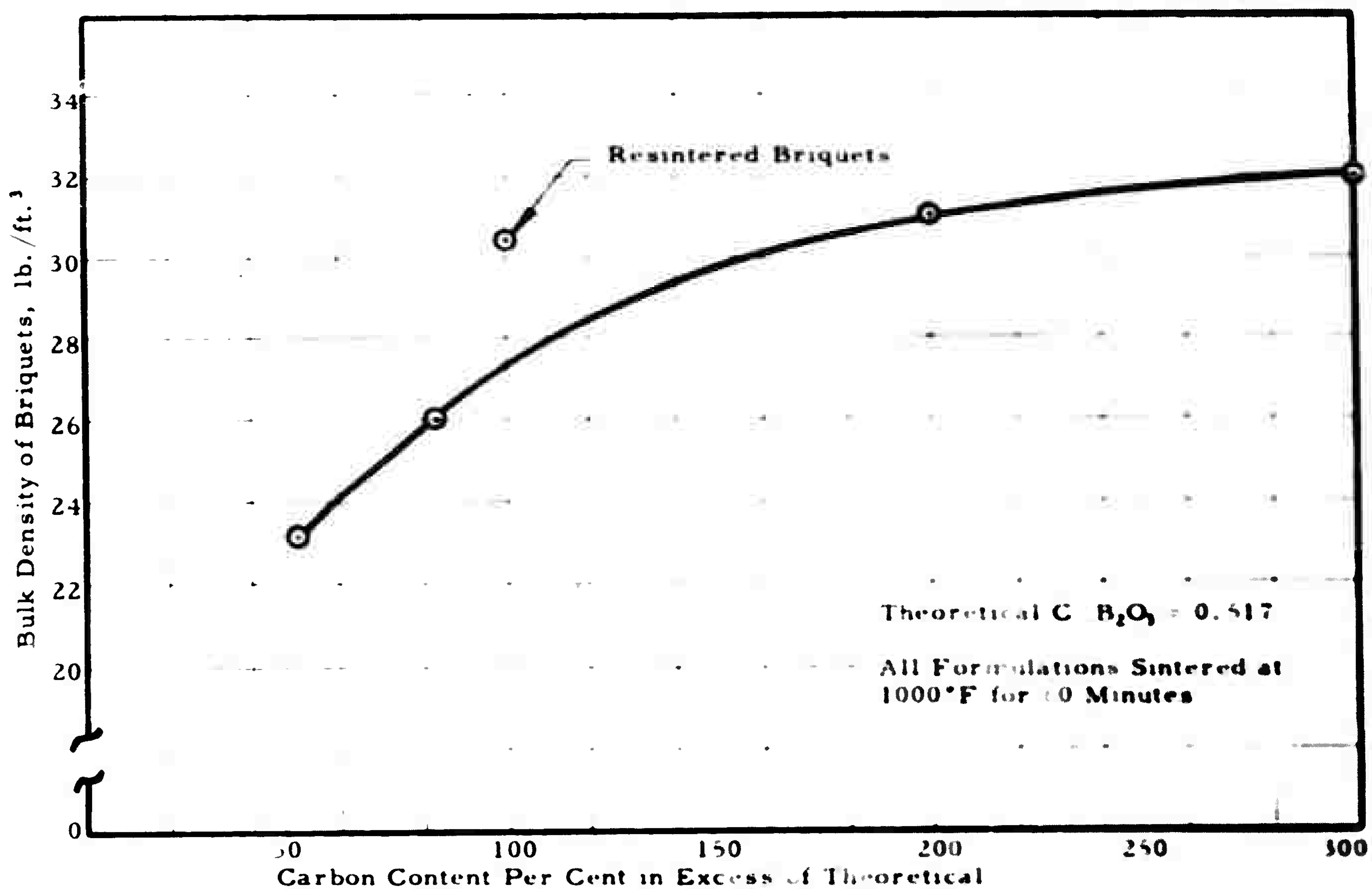


FIGURE 20 - EFFECT OF CARBON CONTENT ON BULK DENSITY OF SINTERED BORIC OXIDE-CARBON BRIQUETS

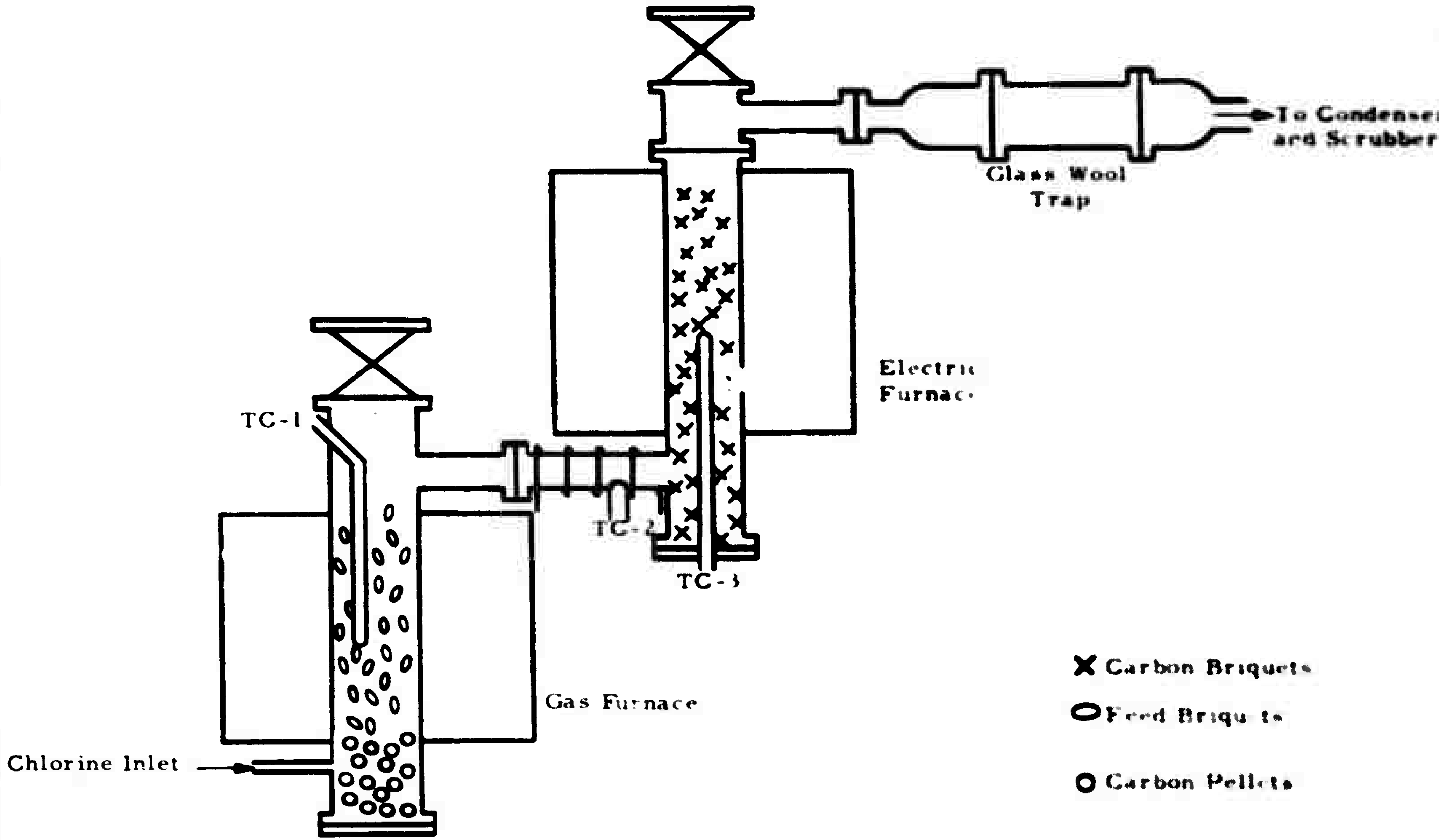


FIGURE 21 - LABORATORY SCALE CHLORINATION REACTOR SYSTEM

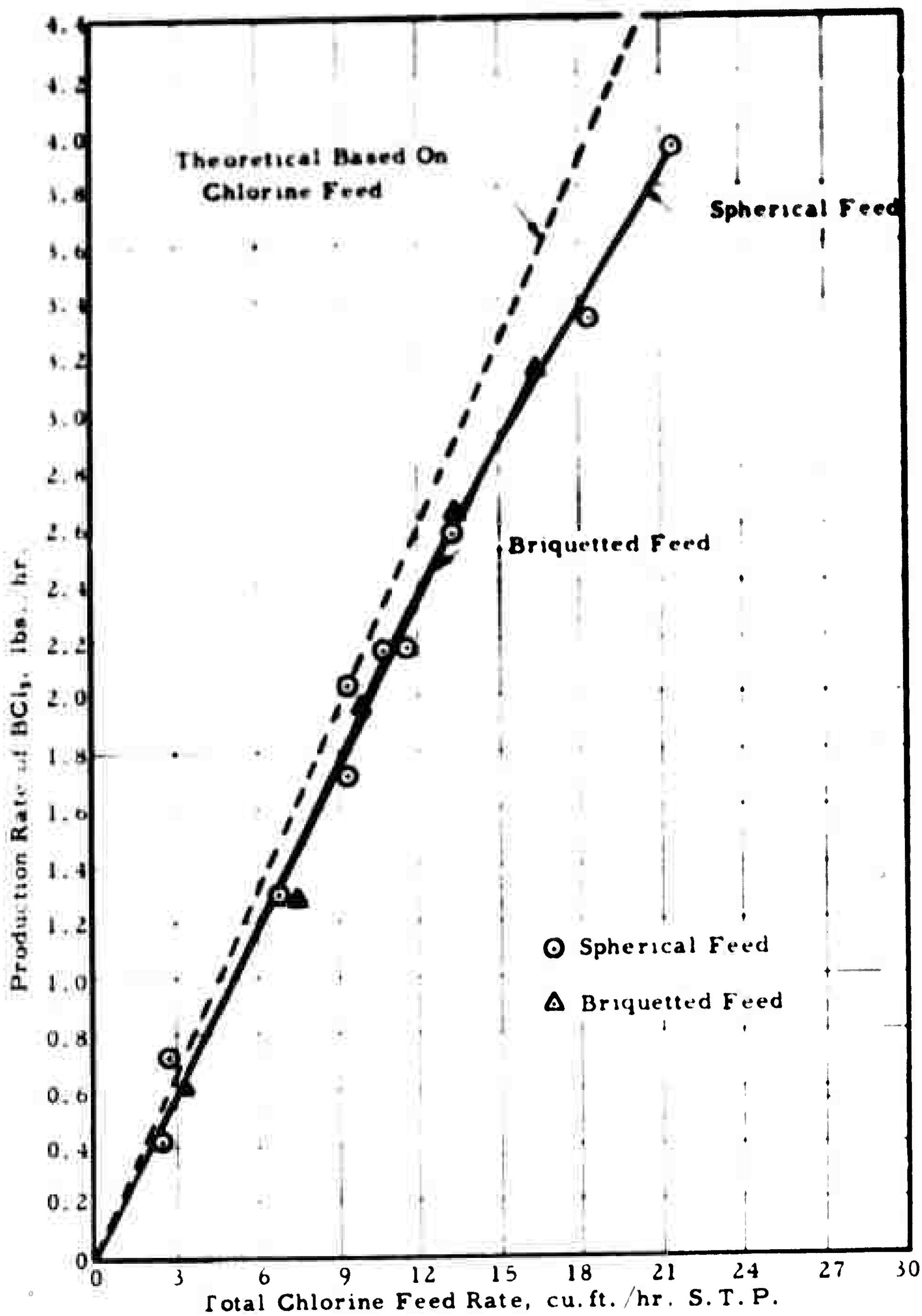


FIGURE 22 - PRODUCTION RATE VERSUS CHLORINE RATE FOR SPHERICAL AND BRIQUETTED FEED

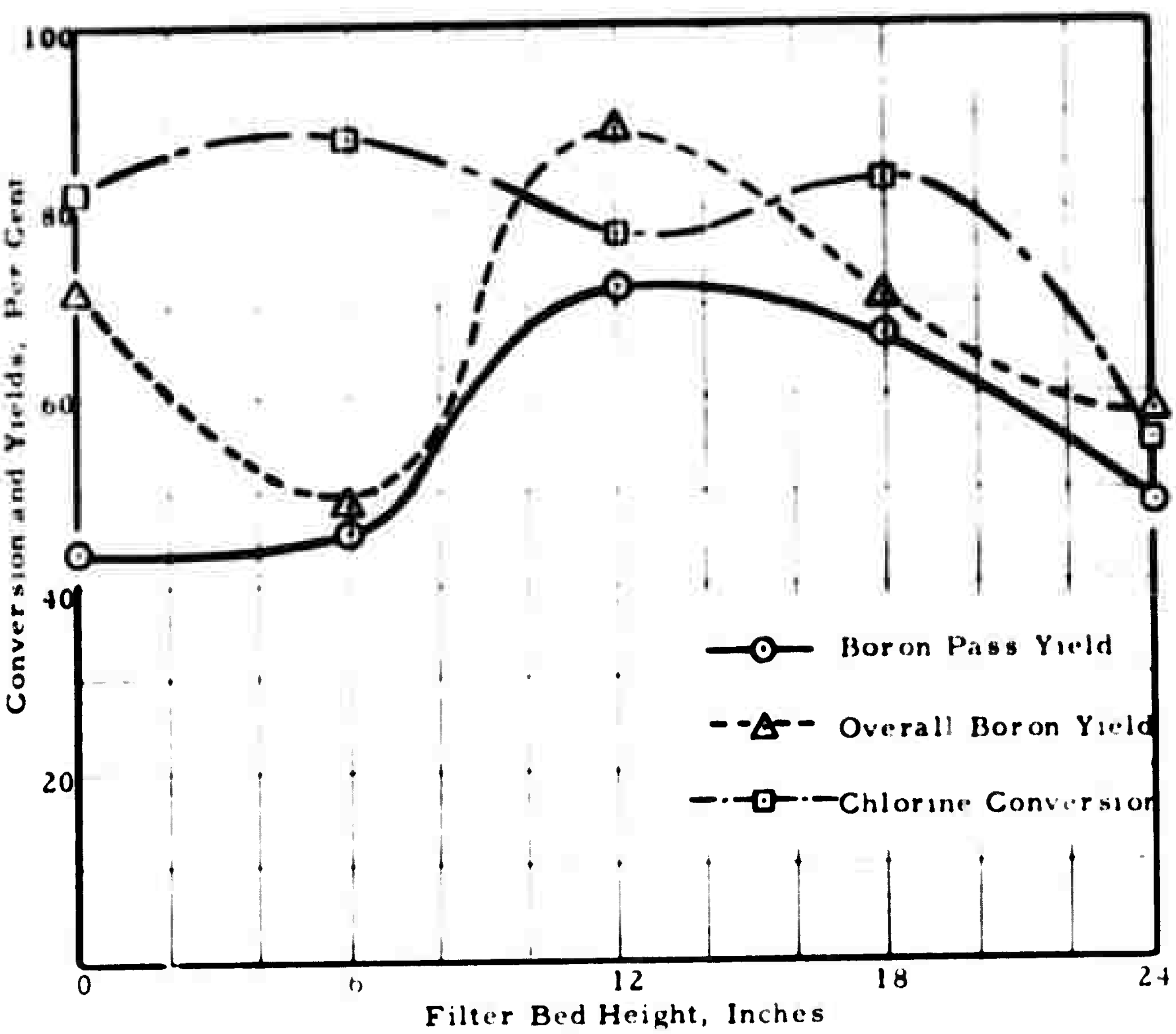


FIGURE 23 - EFFECT OF BORIC OXIDE-CARBON FILTER BED HEIGHT ON YIELDS AND CONVERSIONS

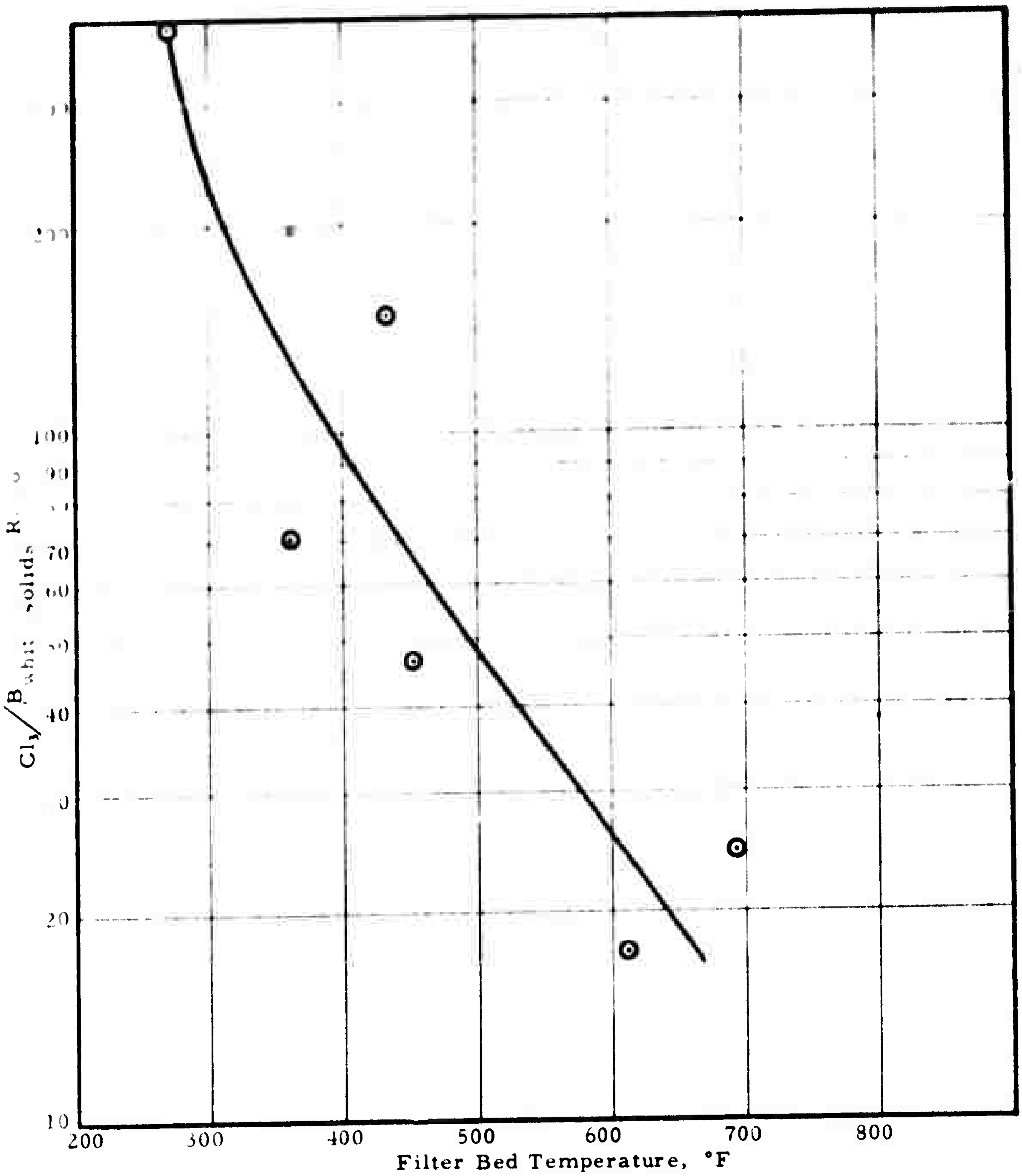


FIGURE 24 - EFFECT OF BORIC OXIDE-CARBON FILTER BED TEMPERATURE ON BORON$_{BCl_3}$ TO BORON$_{White\ Solids}$ RATIO

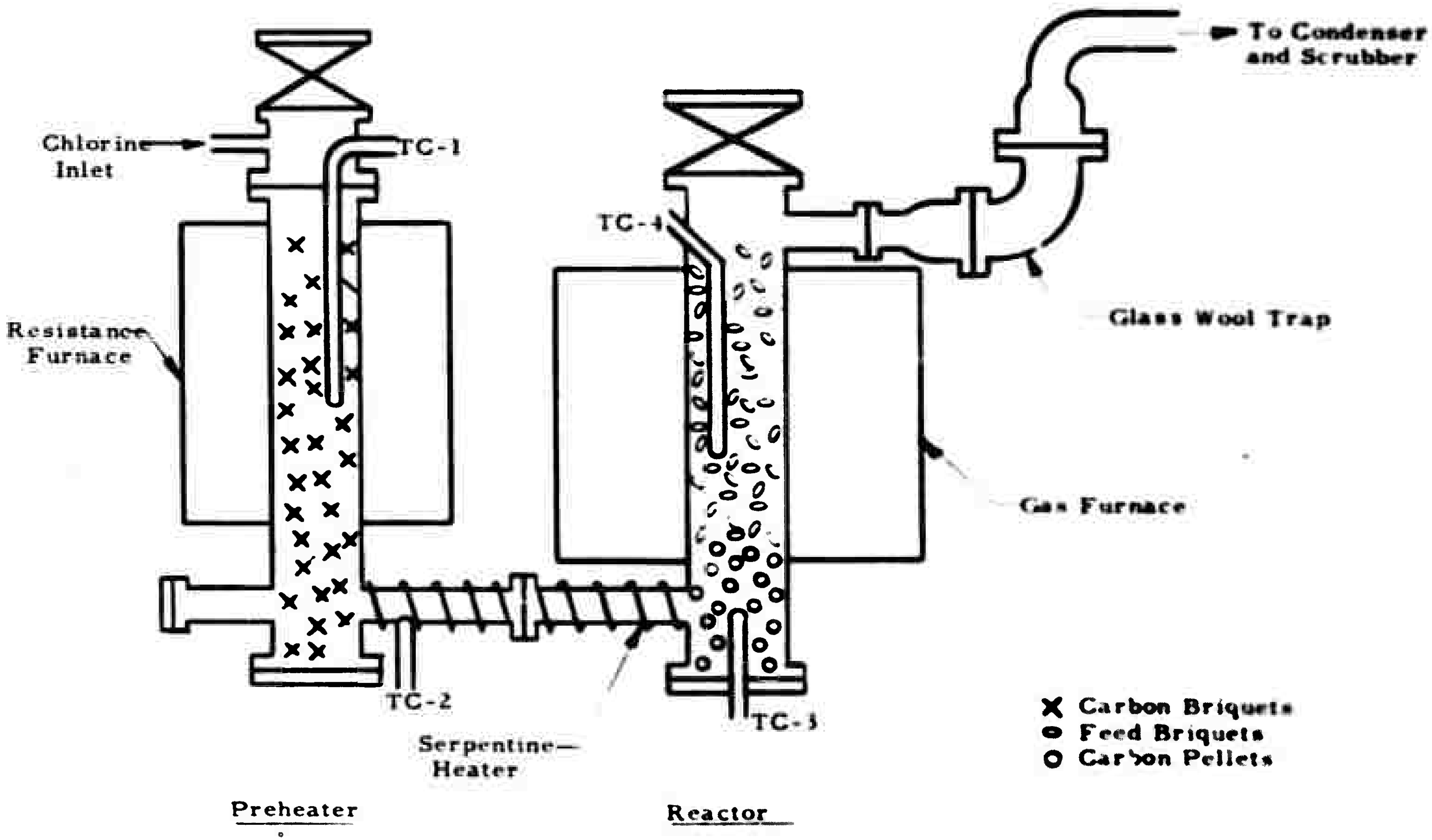


FIGURE 25 - CHLORINE PREHEATER

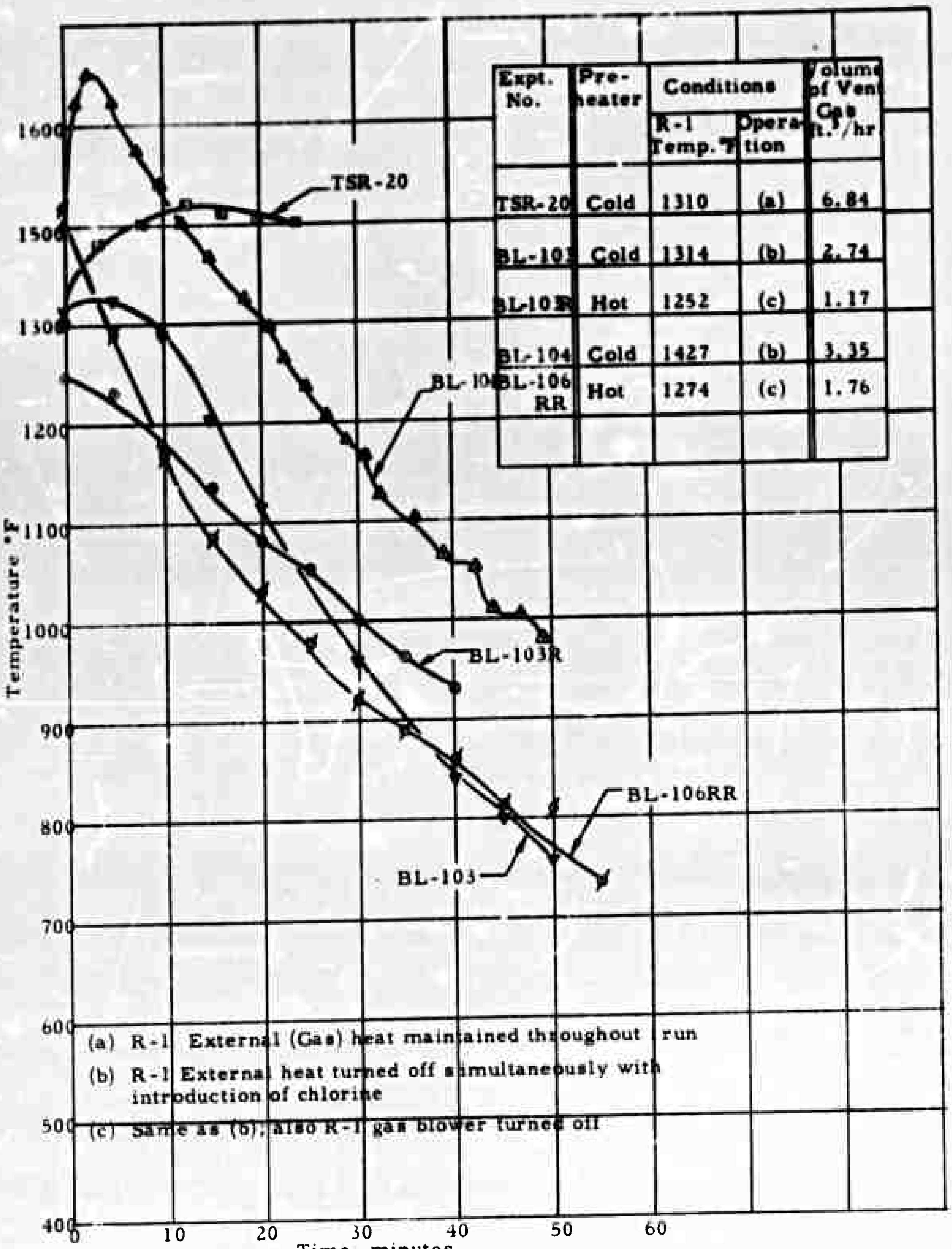


FIGURE 26 - TIME-TEMPERATURE CURVES FOR CHLORINE PREHEATED EXPERIMENTS

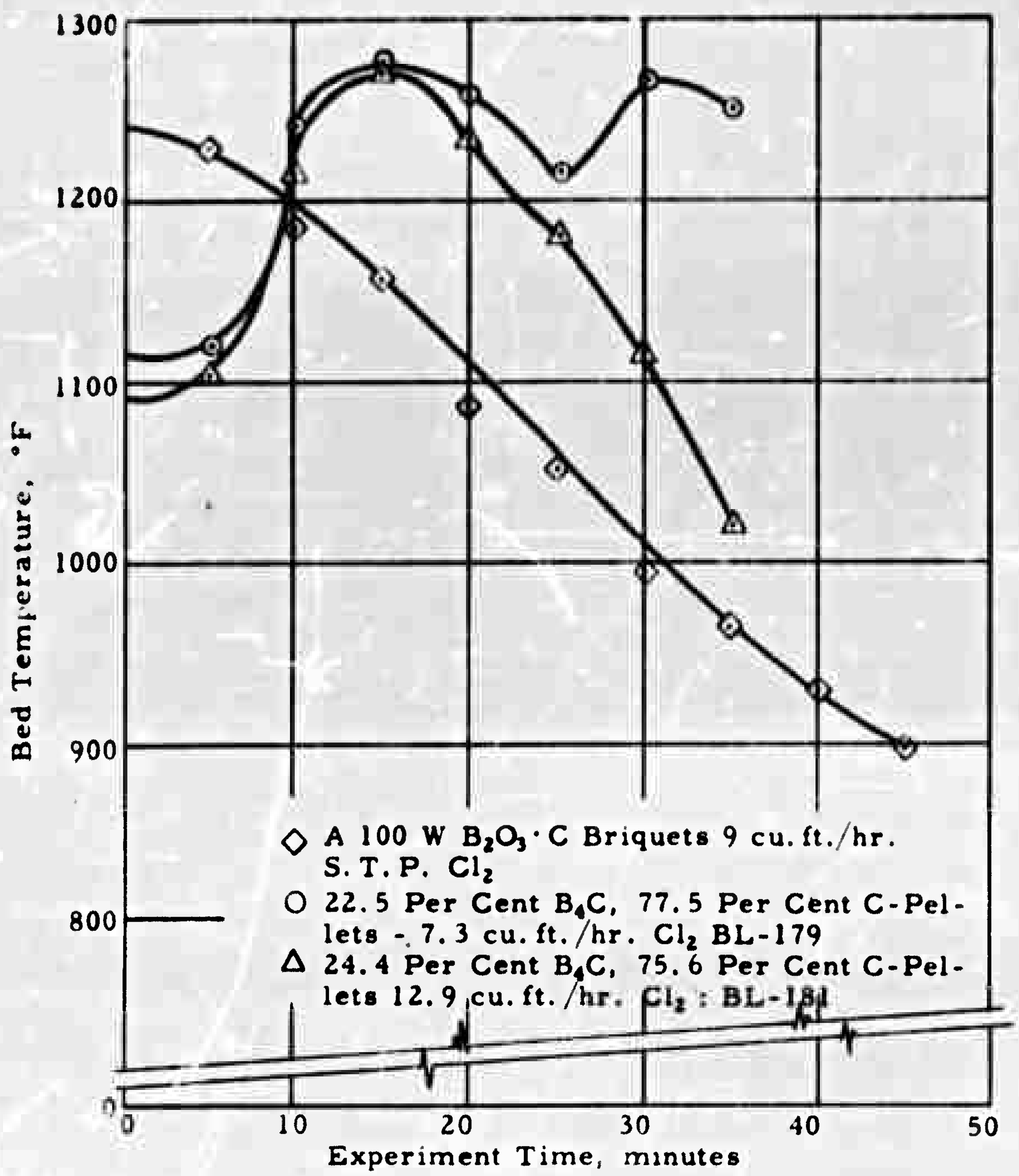


FIGURE 27 - TIME-TEMPERATURE CURVES FOR CHLORINATION OF BORON CARBIDE

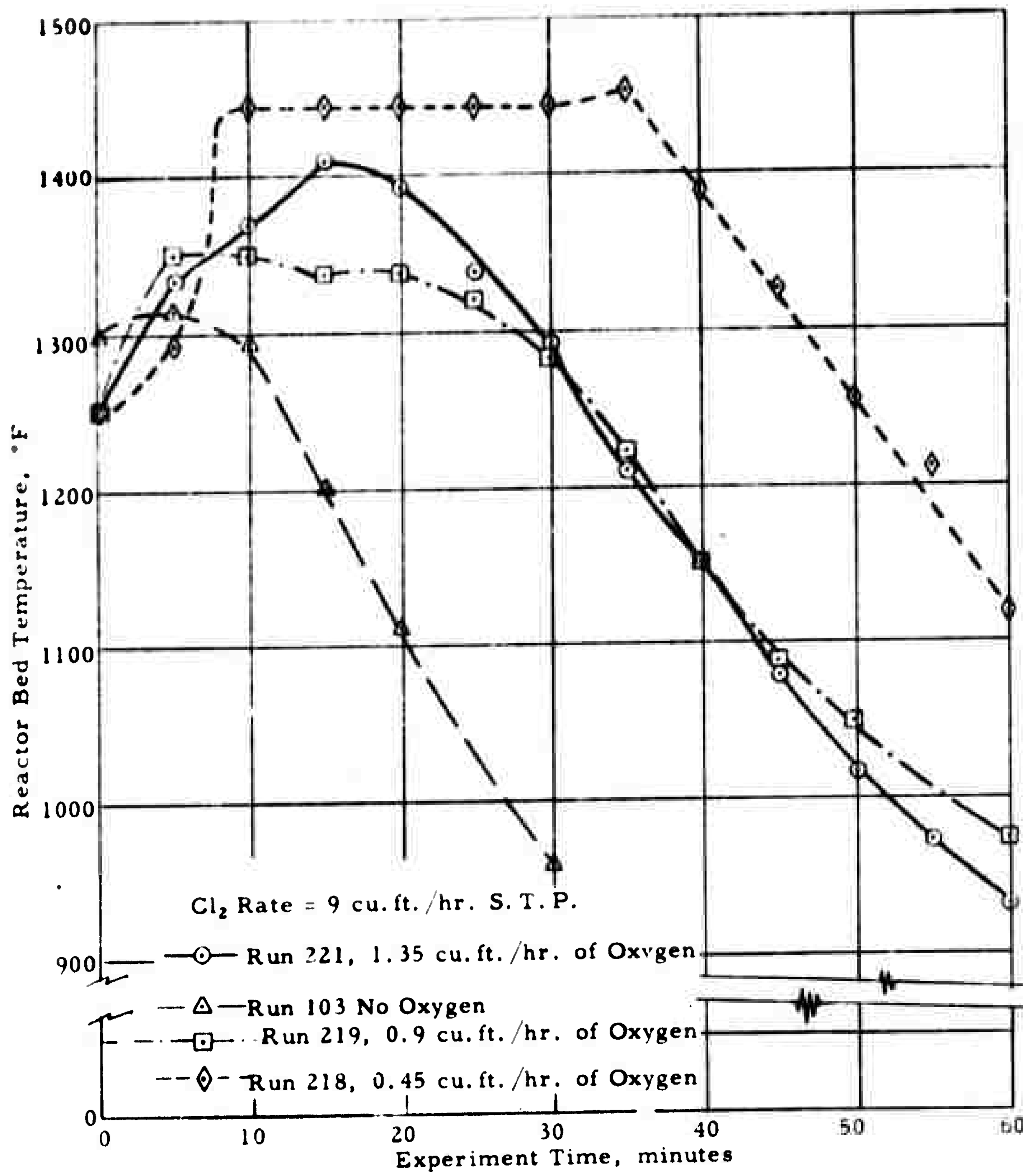


FIGURE 28 - EFFECT OF SUPPLEMENTARY OXYGEN FEED ON REACTOR BED TEMPERATURE

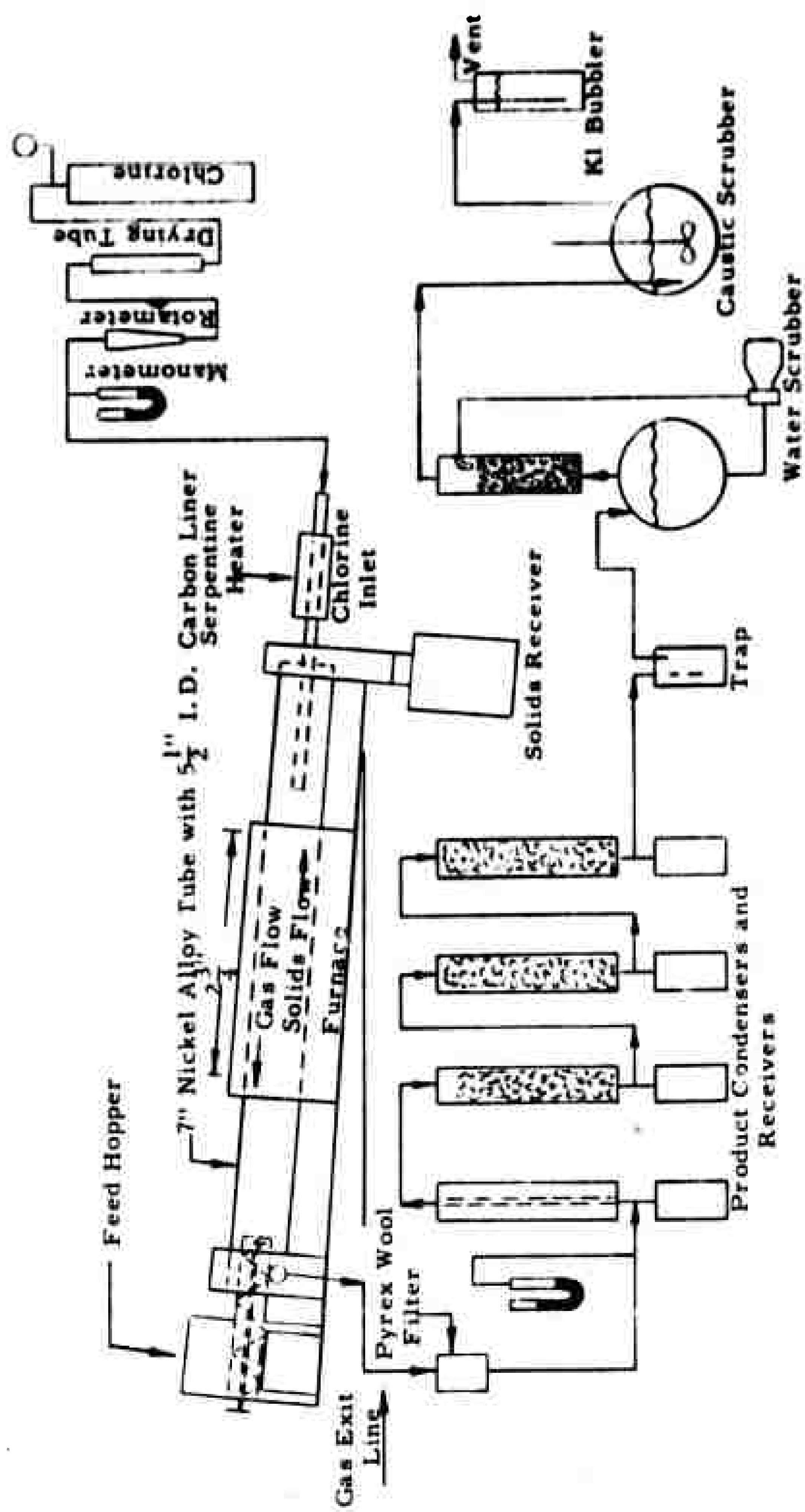


FIGURE 29 - ROTARY TUBE CHLORINATION APPARATUS

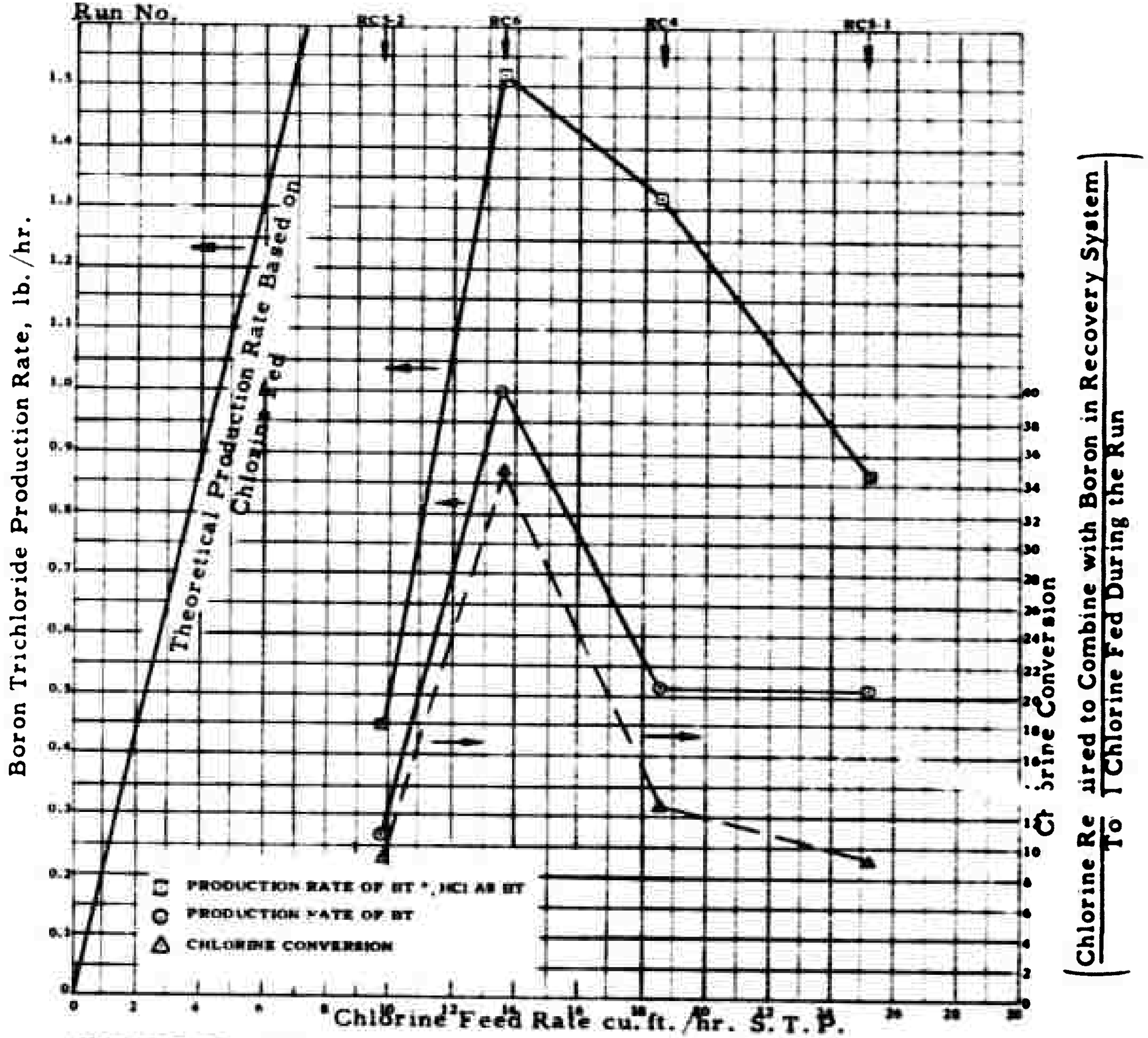


FIGURE 30 - BORON TRICHLORIDE PRODUCTION RATE AND CHLORINE CONVERSION VERSUS CHLORINE FEED RATE

AD 200541

Armed Services Technical Information Agency

ARLINGTON HALL STATION
ARLINGTON 12 VIRGINIA

FOR
MICRO-CARD
CONTROL ONLY

2 OF 2